

## THE ACOUSTICS OF THE ROYAL FESTIVAL HALL, LONDON

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“ . . . . . every soun,  
Nis but of aier reverberacioun,  
And ever it wastith lyte and lyt away;  
Ther nys no man can deme, by my fay,  
If that it were departed equally.”

(The Canterbury Tales, Geoffrey Chaucer, 1340—1400 A.D.)

### Summary

The Royal Festival Hall was opened in London in May, 1951. This paper describes in some detail its acoustical design, the test concerts held in it before the opening, the objective measurements made in it, and the comments about its acoustics that have been made during the first eighteen months since its opening. These comments show that the “definition” is excellent, but that for some types of music more “fullness of tone” would be desirable. It is concluded that the reverberation time is the only objective measurement which, at the present stage of development, is of practical use. Its value in the Royal Festival Hall when full is 1.5 seconds (at 500 c/s), which is 0.2 seconds shorter than the optimum value given by KNUDSEN and HARRIS for a hall of this size. It seems probable that the “fullness” would be adequate if the reverberation time could be lengthened to 1.7 seconds or somewhat longer.

### Sommaire

Le «Royal Festival Hall» a été inauguré à Londres en mai 1951. Le présent article décrit de façon assez détaillée les arrangements acoustiques, les concerts d'essai donnés avant l'ouverture officielle de la salle, les mesures objectives des quantités physiques et les commentaires reçus durant les 18 mois qui suivirent l'inauguration. Ces commentaires indiquent que la «définition» est excellente mais que, pour certains genres de musique, une plus grande «plénitude du ton» serait désirable. Pour conclure, il est établi que le temps de réverbération est la seule mesure qui soit d'utilité pratique dans l'état actuel de la technique. Le temps de réverbération du «Royal Festival Hall» est de 1,5 seconde (à 500 c/s) lorsque la salle est pleine, soit 0,2 seconde en moins que la valeur optima donnée par KNUDSEN et HARRIS pour une salle de cette dimension. Il est probable que la «plénitude du ton» serait satisfaisante si le temps de réverbération pouvait être prolongé jusqu'à 1,7 seconde ou un peu plus.

### Zusammenfassung

Die „Royal Festival Hall“ wurde im Mai 1951 in London eröffnet. In dieser Arbeit werden die akustischen Einrichtungen, die Versuchskonzerte, die vor der Eröffnung stattfanden, die objektiven Messungen und die Beobachtungen über die Akustik der Halle während der ersten 18 Monate ausführlich beschrieben. Diese Beobachtungen zeigen, daß die „Definition“ des Schalles ausgezeichnet ist, daß aber für einige Arten musikalischer Darbietungen mehr Klangfülle erwünscht wäre.

Abschließend wird festgestellt, daß im gegenwärtigen Stadium der Entwicklung die Nachhallzeit die einzige objektive Größe von praktischer Bedeutung ist. Die Nachhallzeit der Royal Festival Hall beträgt bei voller Besetzung 1,5 Sekunden (bei 500 Hz); sie ist also 0,2 Sekunden kürzer als der optimale Wert, den KNUDSEN und HARRIS für eine Halle dieser Größe angeben. Es ist anzunehmen, daß sich die Klangfülle verbessern würde, wenn es möglich wäre, die Nachhallzeit auf 1,7 — oder sogar mehr — Sekunden zu verlängern.

### Introduction

The Royal Festival Hall has been built on the south bank of the Thames under the direction of the Architect to the London County Council, Mr.

Robert H. MATTHEW, and the Deputy Architect, Dr. J. L. MARTIN. Mr. Edwin WILLIAMS was Senior Architect in charge and Mr. Peter MORO associated architect. The acoustic consultant was



Mr. HOPE BAGENAL, in collaboration with the BUILDING RESEARCH STATION (Department of Scientific and Industrial Research). The design work started in August 1948, and the Hall was opened in the presence of Their Majesties King George VI and Queen Elizabeth on 3rd May, 1951.

Concert-hall acoustics is a broad and amorphous subject; it requires a book rather than a paper to deal with it adequately, and this paper is concerned mainly with the practical aspects. The design of the Royal Festival Hall has been described elsewhere [1]...[4] in rather general terms; this paper puts on record in more detail the acoustical design of the Hall, the objective measurements made in it, and the opinions that have been expressed about its acoustics. The hope is that this information will be of help to other designers; certainly the present writers would have been glad of such detailed information on other recent concert-halls.

## 1. DESIGN

### a) Objectives

The Royal Festival Hall (abb. R.F.H.) was designed to accommodate an audience of about 3000, a symphony orchestra of 120 players, a choir of 250 and an organ. Its prime purpose was for symphony concerts; that is to say all other considerations, such as its use for speech, were to be subordinate to the acoustical requirements for music.

Our knowledge of the acoustics of large halls has reached the stage where major faults such as echoes can be avoided in the design, or, failing this, can be eliminated by suitable measures in the completed hall. There remain the very considerable problems of assessing and obtaining exactly the musicians' requirements. In the case of the R.F.H. a determined effort was made to consult the professional musicians. This assessment was made by means of a questionnaire sent to musicians [5], by systematic listening tests in selected concert-halls and by discussions of the problems at public [6] and private meetings with musicians and with other workers in the subject. In addition, and most important, there

was BAGENAL's long and varied experience. It was decided that the most important musical requirements were (i) definition, (ii) fullness of tone, (iii) balance, (iv) blend, (v) no echoes, and (vi) a low level of intruding noise. In addition, it was thought important to obtain reasonably uniform acoustics over the whole audience area.

Some description of these musical terms is necessary. "Fullness of tone" is the most difficult to define, although it is easily recognised. Perhaps all we can usefully say about it is that it is the satisfying quality added to the sounds produced by musical instruments (or voices) when in a concert-hall as compared with in the open air. Although there may be subtle differences, we must assume for design purposes that musicians mean nearly the same quality when they use such terms as warmth, richness, body, singing tone, sonority or resonance. (It should be remembered that "resonance" has different meanings for the

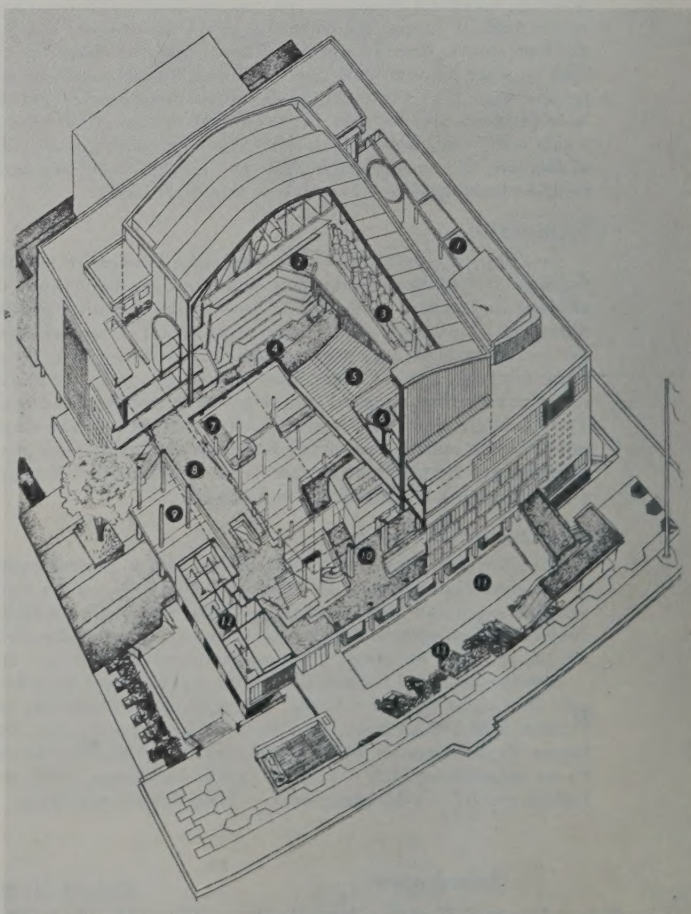


Fig. 1. Axonometric view of Royal Festival Hall (key to relevant numbers: 2 = choir; 3 = boxes; 4 = orchestra; 5 = Stalls; 6 = Grand Tier).



musician and the physicist; the Oxford English Dictionary defines it as the reinforcement or prolongation of sound by reflection.) "Definition" has two main characteristics; the first is concerned with hearing clearly the full timbre of each type of instrument so that they are readily distinguished one from another; the second is concerned with hearing every note distinctly so that, for example, it is possible to hear all the separate notes in a very rapid passage. (Speeds of playing of 15 notes per second are not uncommon.) This implies that the sounds from the whole orchestra should be heard well synchronised. "Clarity" is a term commonly used as an alternative to "definition". "Balance" we would define as the correct loudness ratios between the various sections of an orchestra as heard by the audience. "Blend" is another quality difficult to define, but in general terms it is the possibility of hearing a body of players as a homogeneous source rather than as a collection of individual sources.

part of the paper will state as facts what are only hypotheses. Nevertheless, this part deals with the acoustical design, and these hypotheses are those on which the Hall was designed. The validity of some of the assumptions made will be discussed later.

The basic, obvious, assumptions are that there will be some reverberation and that the audience will receive some of the direct sound from the orchestra. Considering only one aspect of "definition" — speed of playing — it is again obvious and a matter of common experience that a very short reverberation time (abb. R.T.) will not prevent a listener hearing all the rapid notes distinctly, while a very long R.T. will. Further, even in the presence of a very long R.T., definition is still maintained when the listener is very close to the source. Assuming for the moment that a very short R.T. is not desirable in a concert-hall, it is a simple conclusion that the intensity of the direct sound must be as great as possible. Now

the intensity of the direct sound reaching the listener will fall off as the square of the distance, at least for individual instruments if not for the whole orchestra, and in a hall of the size of the R.F.H. the difference in intensity level between the front and back rows would be about 20 dB. (In the Chaucer quotation at the head of this paper, the word "departed" means, in modern English, "divided".) HAAS [7] has recently put on a quantitative basis what has long been assumed, namely, that for speech at least, reflections following shortly after the direct sound do not detract from the definition. For example, reflections of the same intensity may be delayed

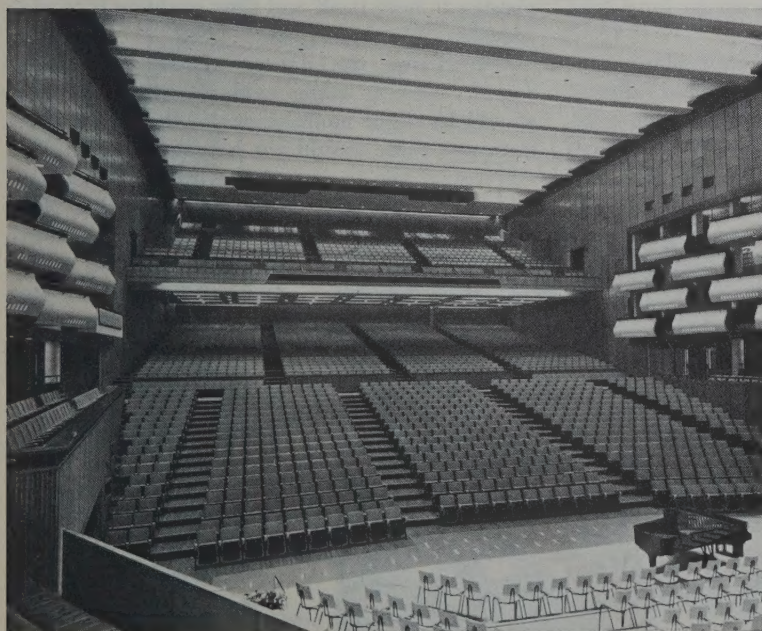


Fig. 2. Auditorium of Royal Festival Hall.

For design purposes we must rely on geometric and statistical acoustics: solutions in terms of wave acoustics are not yet possible even if all the physical factors were known. For example, it would be difficult to derive a mathematical expression for the shape of the boxes in the R.F.H. (Fig. 2).

To avoid the too frequent use of such cautionary clichés as "it appears to be the case", this

up to about 30 ms behind the direct sound without any loss of definition. The conclusion is that to maintain definition over the whole audience area, short-path reflections directed towards the rear of the hall should be used to help the intensity of the direct sound.

It is true that the foregoing simple argument is based on geometric acoustics and also takes no account of the many remarkable properties of the



ear such as its ability to discriminate against unwanted sounds. Nevertheless, in the absence of positive evidence to the contrary, these suppositions form a reasonable basis for the design of a hall.

There remain the problems of obtaining "fullness of tone", "balance" and "blend". "Balance" is partly a matter for the conductor, and is discussed below in connection with platform design. As for "fullness of tone", it is very difficult to decide what acoustical factors control this quality. Certainly the only factor we have under any control is the reverberation, and the most reasonable supposition is that the longer the R.T. the more chance there is of obtaining fullness. It may be that, for a given R.T., the lower the intensity of the direct sound the more fullness there will be, but without reflecting surfaces it is certain that we shall have less uniformity over the audience area. Under present conditions it is better to aim at uniformity and therefore to use surfaces close to the orchestra to reflect sound towards the back of the hall and, for fullness, to design for a long R.T.

If the above argument is correct, it follows that there is a conflict between definition and fullness. Obviously the definition will suffer in the presence of a very long R.T. and vice-versa, although

there may be a range over which fullness can be increased without any noticeable loss of definition. The opinion survey [5] referred to above showed that Liverpool New Philharmonic Hall had by far the best reputation for good acoustics of any concert-hall in Britain, and listening tests made in this hall showed that its definition was good. On the other hand, at a meeting of the Acoustics Group [6] the consensus of opinion among musicians was that definition should, if necessary, be secondary to fullness. As it is comparatively simple to shorten the R.T. of a hall, it was decided to design the R.F.H. for as long an R.T. as possible.

"Blend", like "balance" is partly a matter for the conductor, but is probably best helped by surfaces close to the orchestra which reflect some of the sound directly back to the orchestra. These surfaces should help in two ways: (i) by "mixing" some of the orchestral sound before it reaches the audience (the extreme example is the Prinzregent Theatre in Munich) and (ii) by helping the orchestra to hear itself and thus enabling it to play together.

Considering the nature of the reverberant sound, there is some evidence [8] that there should be slight modulations of the decay. That is to say, there should not be complete diffusion of the reverberant sound field. On the other hand some diffusion is of course inevitable and, no doubt, desirable. But again no quantitative data were available.

#### b) Shape on plan

The three possible basic shapes of a hall are horseshoe, fan or rectangular. The horseshoe shaped hall is theoretically dangerous acoustically because of the concave surfaces involved, although in the past some successful halls have been built in this way, e.g. Usher Hall, Edinburgh. Nevertheless the dangers involved are too considerable to be ignored, and the choice then is between a fan shaped and a rectangular hall. The main advantage of the fan shape is that the length of the

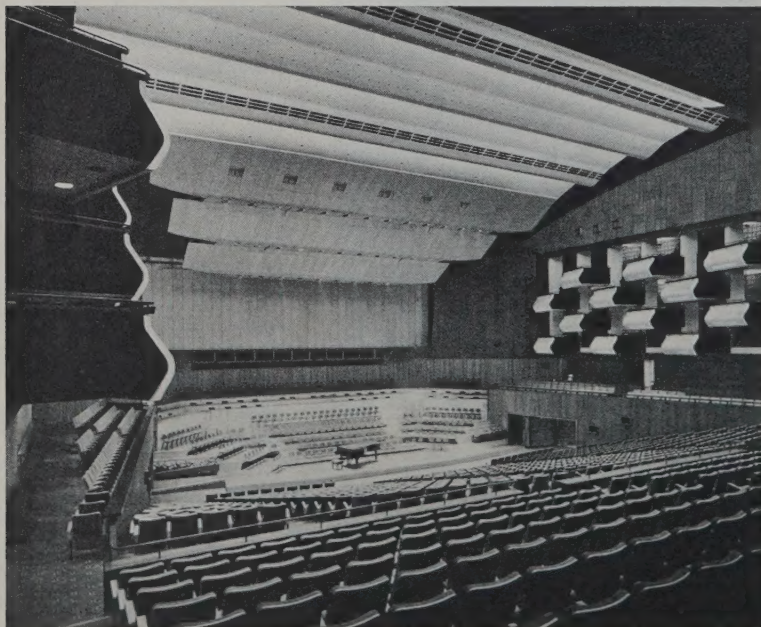


Fig. 3. Orchestra platform of Royal Festival Hall (Note: the platform is arranged for a violin recital, with seats for audience. The temporary organ screen referred to in the paper has been replaced by the permanent, openable, screen).



hall is less than that of a rectangular hall seating the same number and of the same width at the orchestra end. The main disadvantage is that the rear wall, balcony front and seat risers are all curved causing a serious risk of echoes. The rectangular hall is almost free from this risk, and in addition has a possible advantage that there is more cross-reflection between the parallel walls which may give added "fullness". These two considerations, plus the weight of tradition, led to the adoption of a rectangular shape for the R. F. H., although of course the arguments are not conclusive. To overcome the main disadvantage of a rectangular hall — its large width at the orchestra end — the seating at the front part of the R. F. H. was made fanshaped at the orchestra level (Fig. 4).

the orchestra is not quite so difficult if the area of the sound source is small. It is more important to keep the depth of the platform to a minimum, rather than the width. This is because the time delays from front to back of the platform are heard by the whole audience: the time delays due to the width affect a relatively small proportion of the audience, although they do affect instruments widely separated from each other and consequently not easily heard by each other.

In longitudinal section, an orchestra platform can be (i) flat, (ii) flat for the front part and raked for the back part or (iii) completely raked from front to back. With designs (i) and (ii) the weakest instruments — the wood-wind — are screened by the players in the front of the orchestra, and, in design (ii) the most powerful instruments — the

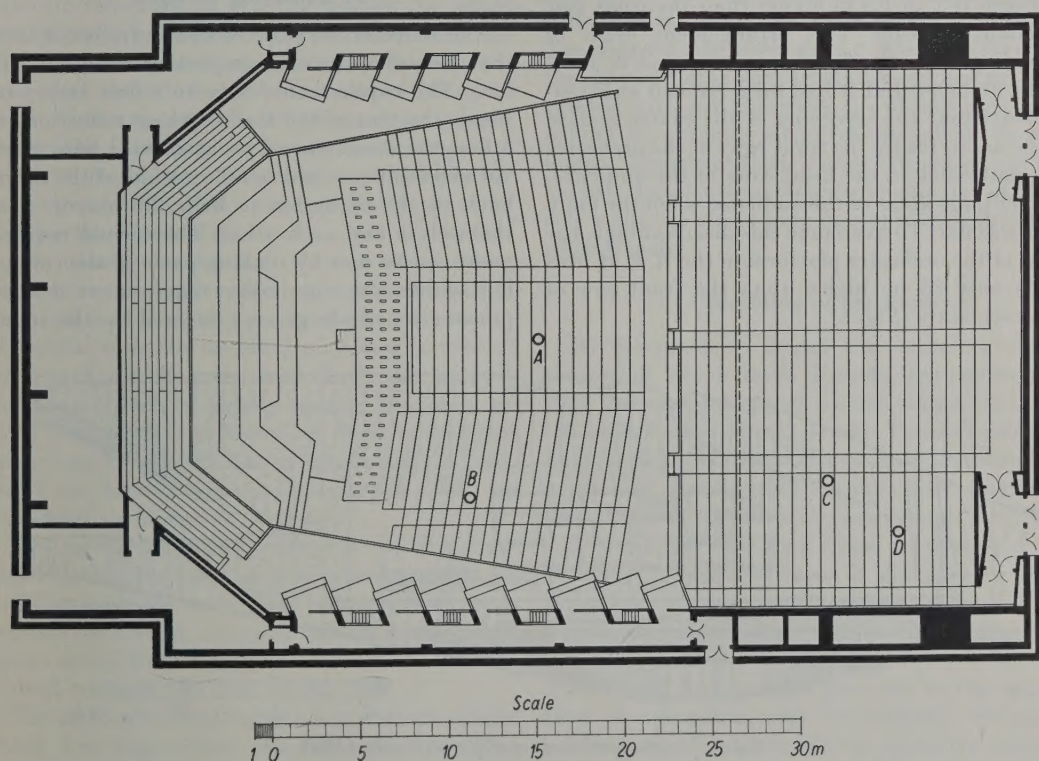


Fig. 4. Plan of Royal Festival Hall.

### c) Orchestra and choir platform

The area of the orchestra platform should be as small as is consistent with adequate room for the players, since the time delays between the various sections of the orchestra should be kept short, thus aiding definition and homogeneous playing. Further, the design of the reflecting surfaces close to

brass and percussion — have an advantage which they do not need. Design (iii) was adopted for R. F. H., with all instruments exposed more or less equally. It is true that the powerful instruments are still unnecessarily exposed, but with all instruments given an equal chance it can then be left to the conductor to achieve the correct balance.



The platform in the R.F.H. was constructed of birch on timber framing, with some absorbent material under the platform. The back tier was built of birch fixed solid onto concrete to prevent the timpani setting the whole platform into vibration. To save space, most of the music stands were mounted on tracks instead of the usual tripods, the average area per player being  $1.5 \text{ m}^2$ . The choir seats were placed in rows at the back and sides of the orchestra. The organ consultant required an unobstructed opening for the organ of 18 m horizontally by 9 m vertically. Because of this requirement the platform (including the choir seats) had to be wider than was desirable for purely orchestral or choral purposes.

#### d) Longitudinal section

In most concert-halls the front of the orchestra platform is 1 to 1.5 m higher than the front row of audience seats. This arrangement helps to provide good paths for the direct sound to most of the audience but it had been noticed at listening tests that the screening of the centre section of the orchestra by the front rows of the orchestra was noticeable in the front rows of the audience, or over large areas of the audience when the main floor was flat. To overcome this disadvantage, the front of the orchestra platform in the R.F.H. was made only 23 cm higher than the front row of audience seats (Fig. 5).

reasons. The ceiling was intended to be of solid fibrous plaster, 5 cm thick, but during its construction (it was prefabricated in sections and then brought to the Hall for erection) its thickness was, by mistake, reduced to 1 to 2 cm. After erection in the Hall its thickness was made up to the specified 5 cm but using vermiculite plaster instead of the specified fibrous plaster. This slip in the close liaison maintained between the consultants and the architects was a little unfortunate in that, as described later, it probably helped to make the ceiling more absorbent than was intended.

#### e) Cross-section

The ceiling, and of course the floor, are horizontal in cross-section.

#### f) Reflecting surfaces

The reflector over the orchestra (referred to as the canopy) is the most important reflecting surface. The requirements were to reflect sound towards the rear of the Hall — these reflections to follow the direct sound by as short a time interval as possible — and to reflect some of the sound back to the orchestra to help the players hear themselves and each other. The second requirement can be met by making parts of the canopy horizontal but the main requirement is complicated by the large area covered by the sound

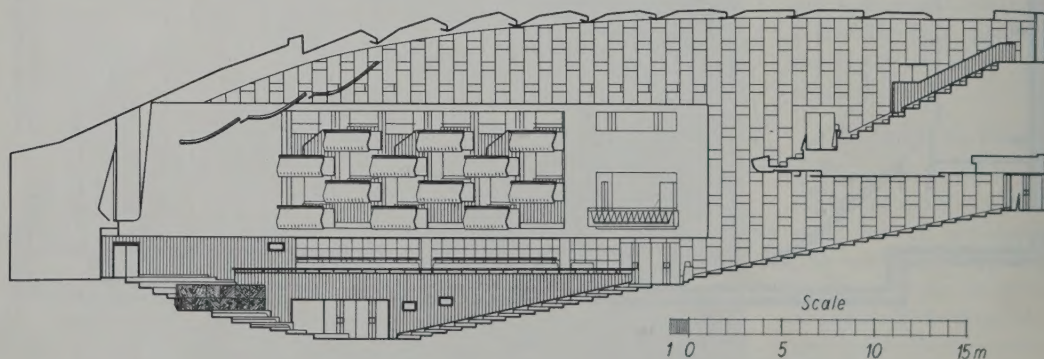


Fig. 5. Longitudinal section of Royal Festival Hall.

The raking of the floor area had been calculated [9] on the basis of a free height of 8 cm between successive rows. However this rake differed so little from a straight line that the considerable extra expense and inconvenience (e.g. varying step height) was not considered worthwhile and a straight line was adopted.

The ceiling follows a general line designed to reflect sound towards the rear of the Hall. The small undulations are for lighting, not acoustical

source. It is clear that an angle for the canopy suitable to reflect instruments at the front of the orchestra towards the rear of the hall is not suitable for instruments at the back, and vice-versa. Consideration of the design actually used will help to illustrate the problems. The height of the rear leaf of the canopy was set by the demand of the organ consultant for a free opening for the organ 9 m high. This leaf reflects sound from the choir and the rear instruments of the orchestra towards



the rear of the hall. On the other hand, sound from the front instruments is reflected straight back to them. If the angle of inclination to the horizontal of this leaf were increased to reflect the front sound more towards the rear of the hall, not only would the rear instruments be reflected to the ceiling but the other leaves of the canopy would have to be higher since the back point is fixed in space. The front leaf reflects the front instruments' sound towards the rear but the back instruments' sound towards the ceiling; a reduction in the angle of inclination in order to help the back instruments would tip the front instruments' sound too much towards the floor area.

There is a further consideration: while at middle and high frequencies the dimensions of each leaf of the canopy are large compared to the wavelengths and can therefore be considered as separate reflectors, at low frequencies the whole canopy must be considered as one reflector. Thus if the angles of inclinations of the leaves were such that the whole formed a concave surface, some focussing of the low frequencies would occur. The focussing might only occur at points in space where there is no audience, but we are not yet so confident in acoustical design as to be able to take such risks.

The canopy in the R.F.H. is a compromise between the various conflicting requirements. The front leaf is at a slightly greater inclination to the horizontal than the middle leaf, which in turn is more inclined than the back leaf: the general contour is therefore slightly convex. It is made of wood 5 cm thick: the leaves are fixed by resilient mountings to timber beams which hang by tie rods from the roof trusses. Its weight is 12 000 kg plus 3 000 kg of lighting fittings.

The second reflecting surface is the flat floor area between the front of the orchestra platform and the audience seats. This reflector is of slate bedded solid onto concrete, and is intended to reflect sound from the front instruments, i.e. the violins, towards the rear of the Hall.

The third reflecting surface is a wooden screen about 1 m high which separates the orchestra from the choir seats. The walls splayed on the plan are a fourth group of surfaces; they are made of wood 1 cm thick on 10 cm battens with absorbent in the air space. Some diffusion was introduced on these splay walls in the form of protruding triangles.

The organ was not to be installed for some time after the opening of the R.F.H. and in the meantime the opening for the organ was covered by a wooden reflector set at an angle of  $15^\circ$  to the vertical (Fig. 5).

### g) Echoes

The three areas considered most likely to cause echoes were the rear wall, the margins where the side walls meet the ceiling, and the side walls near to the orchestra. The risk from the rear wall was slight: the wall was not curved and its area was comparatively small. The treatment applied to it was therefore only slightly absorbent at mid and high frequencies, although these areas were used to provide additional low-frequency absorbent. It consisted of leather "cushions" stuffed with glass wool and mounted on 10 cm battens with rock wool in the air space. Identical treatment was used on the side walls below the boxes and on the door lobbies at the entrances either side of the orchestra. The margins were made of unplastered wood-wool slabs on battens, the vertical and horizontal parts each being about 1.5 m wide, and ran along the whole length of the Hall. The splayed side walls next to the floor level for the first 10 m away from the orchestra were treated with slit absorbers which had rock wool behind wood facing strips (the so-called "Copenhagen" absorbent from its use in the foyer of the Danish Broadcasting House); for the rest of these side walls the strips were mounted straight on to wood panels.

### h) Prevention of resonances

By resonance is meant the excessive accentuation of one or more discrete frequencies and their associated decay at a much slower rate than the general reverberant sound. These resonances may occur in two ways: by room eigentones between, say, two parallel surfaces with small absorption, or by mechanical resonances of a surface, e.g. a panel. The first type is described by JORDAN [10] and was cured in that case by using Helmholtz resonators. The ceiling of the R.F.H. was made with about 1200 holes 5 cm in diameter for use with resonators if needed. The surfaces in the R.F.H. which might give rise to the second type of resonance were the ceiling, the wood panels on the side walls and the orchestra canopy. The ceiling and the canopy were constructed in different sized sections which were then butted together with a strip of soft fibreboard between. A wood panel of the type to be used on the side walls was tested for its decay rate in the laboratory; at its resonant frequency the decay was found to be about 250 dB/s with absorbent in the air-space and about 100 dB/s without absorbent. Both these decay rates were much faster than the expected reverberant sound decay.



### i) Reverberation time

The aim was to achieve as long a reverberation time as possible (at mid-frequencies). At an early stage in the design a R.T. of 2.2 s was considered, being the value recommended by BAGENAL and WOOD [11] for a hall of the volume of the R.F.H. As the design developed, and as results of measurements in other British concert-halls became available [5], it was realised that this value was unlikely to be reached: the volume per seat would have been excessive with corresponding troubles with echoes from remote surfaces. A calculation of the R.T. as the design progressed gave a value of 1.7 s at 500 c/s. It was not possible to increase this figure: the volume per seat could not be increased, e.g. by increasing the ceiling height, for structural reasons, nor could the number of seats be reduced; the absorbent areas had been kept as small as possible (except for a small area of carpet required by the architect) while still preventing echoes. This value of 1.7 s is that recommended by KNUDSEN and HARRIS [12] for a hall of this volume, and as several good British concert-halls had been found to lie close to or below the KNUDSEN and HARRIS optimum it was thought to be acceptable.

At high frequencies the R.T. is largely controlled by air and audience absorption, and the designer can do nothing about it. At low frequencies however, there is a danger that the R.T. may be too long. In traditional constructions there are large quantities of fortuitous low-frequency absorption in the form of plaster panels, etc.: in modern constructions of reinforced concrete and with little ornamentation this absorption may not be present. The designers had always in mind a small concert-hall built in the 1930's of reinforced concrete: the R.T. at low frequencies was 13 s, and the hall has now been converted into offices. The calculation of R.T. at mid-frequencies is uncertain; at low frequencies the uncertainties are worse because of the lack of information on the absorption of surfaces at these frequencies. For example, the absorption coefficient at 125 c/s of the ceiling (5 cm thick with an air-space 4 m deep behind it) might have been anywhere in the range 0.05 to 0.4. The major risk therefore was that the R.T. at low frequencies would be too long: the designers would have been satisfied at the design stage if the R.T. at 125 c/s would come in the range 1.7 to 2.5 s, i.e. between 100 and 150 per cent of the value at 500 c/s. A conservative estimate of the absorption to be expected from the various surfaces and audience was made for 125 c/s; a sufficient area of wood

panels spaced from the wall was included in the design to ensure that the R.T. was not too long. As the majority of absorption might thus have been expected to be due to these panels, their construction was varied to ensure that absorption was not concentrated over a too narrow band of frequencies. The construction and absorption coefficients of these panels have already been described [13].

It is desirable for the orchestra that the acoustics in a concert-hall should not be too different under performance and rehearsal conditions. It had been noted that the R.T. in empty concert-halls was between 10 and 75 per cent longer than when the halls were full [5]. The tip-up upholstered seats for the R.F.H. were designed with the underside of the seat perforated, with rock-wool behind the perforations.

### j) Sound insulation

It is intended to describe the sound insulation of the R.F.H. in more detail elsewhere. Briefly, the two major sources of noise at the site were overground electric and steam trains running on the nearby Hungerford Bridge, and the underground trains running directly under the site. The noise from the overground trains was measured at various positions on the site, and a wall and roof construction for the auditorium was devised sufficient to reduce these noise levels to the background noise levels measured in two other concert-halls during pauses in quiet passages of music. The wall construction consisted of two leaves of re-inforced concrete each 25 cm thick separated by an air-space 30 cm wide, with some absorbent in the air-space. The roof construction consisted of an inner leaf of reinforced concrete 15 cm thick carrying sleeper walls which varied from 60 cm to 120 cm high (depending on the camber of the roof). Over the top of the sleeper walls was draped a 5 cm layer of glass-wool and the outer leaf of 10 cm of reinforced concrete rested on this. All doors except two into the auditorium were built with sound locks, and the two exceptions (in the final design) had extra precautions taken in the foyers leading to them.

At this stage of the design it was necessary to give the architects as much freedom as possible in the positioning of the auditorium, and the constructions specified were intended to give adequate insulation on their own. In the event, most of the auditorium was enclosed by foyers, corridors, etc. all of which were designed to give extra insulation, both as an added safeguard and as an aid to reducing the noise level below that measured in the two other halls.



The ground vibrations due to the underground trains were measured and were thought to be sufficiently small not to produce troublesome noise in the auditorium. As a safeguard the auditorium was placed as high above ground level as possible.

The inlet and outlet ducts for the ventilation plant were treated to reduce the external noise by the same amount as the walls and roof, and the plant itself was designed for minimum noise.

### k) Capacity

The final figures for the capacity of the R.F.H. are as follows:

#### Seating:

Orchestra	about 125
Choir	248
Stalls	663
Terrace Stalls	1120
Grand Tier	616
Side Balconies	152
Boxes	200

#### Standing:

Side Balconies	120
Sides of Terrace Stalls	80
Behind Terrace Stalls	24
Behind Grand Tier	56
Total	3404

The volume is  $22000 \text{ m}^3$  so that the volume per person when the Hall is completely full is  $6.4 \text{ m}^3$ .

## 2. TEST CONCERTS

The first purpose of the test concerts which were held in the R.F.H. prior to its opening was to test for major faults such as echoes. Any faults which might have been found could then have been investigated and remedied before the public opening. Reliance was placed mainly on subjective listening tests; only limited objective measurements were possible with an audience present, and in any case even obvious faults such as echoes cannot be assessed with much reliability from objective measurements. At the first test concert, on 14th February, 1951, there were two classes of listeners in addition to the normal audience. The first class consisted of 13 groups of 20 listeners each distributed over the whole seating area. These were classified as ordinary concert-goers, and had all been to at least six concerts in the previous year. They answered questionnaires which dealt with such subjects as noise, echoes and loudness. The second class consisted of six groups of two or three people each who had some knowledge of acoustics and most of whom had

already taken part in similar tests in other concert-halls. Each group of "specialists" sat in different positions in the Hall for each of the three parts into which each test concert was divided. These positions were B, C and D as shown in Fig. 4, and symmetrical positions on the other side of the centre-line of the Hall. Their function was to give more detailed reports on the acoustics and on the variations between positions; for example if echoes had been heard they would have been expected to estimate the probable source.

It was clear at the first test concert that there was only one major fault. The group of 20 at the extreme back of the Grand Tier had behind them an absorbent gangway which had a wood-wool ceiling and the leather-panelled rear wall; this group gave less favourable answers, on the whole, than the other groups. As examples: in reply to the question "Was it easy to listen attentively?", 95 per cent of all the other groups answered "Yes" compared with 70 per cent for this group; in reply to the question "Were crescendos effective?", 80 per cent of all the other groups answered "Yes" compared with 35 per cent for this group. Before the next test concert the wood-wool ceiling of this gangway was plastered over; this group then gave answers similar on the average to the other groups.

Attention was subsequently concentrated on the proper balance between fullness of tone and definition. The majority of both classes of listeners at the first test had said that more fullness was required; accordingly some absorbent was removed, as described in Part 3, before the second test concert on 14th March. At this second test and at the final test on 15th April — there was an extra test on the 18th March which was held for non-acoustical reasons and which need not concern us here — a third class of listeners was used, consisting of professional music critics who, like the second class, were divided into three groups sitting in different positions (B, C and D) for each part of the tests.

It will be simplest if the main result of these subjective tests is stated first. This was that the absolute opinions on the acoustics were not consistent. For some reason, possibly because of the effect of listening mainly in the Royal Albert Hall for ten years, most of the listeners found the acoustics of the Royal Festival Hall rather surprising, at a first hearing. This is best illustrated by considering the replies of the professional critics. At the first concert they attended, on the 14th March, 10 out of 14 critics wanted more fullness of tone, three wanted more definition and one wanted the Hall left as it was. At the next



concert they attended, on the 15th April, nine of these 14 wanted the Hall left as it was, three still wanted more fullness and two wanted more definition. Now it is seen from Table II that the R.T. was practically the same at these two concerts. Although the R.T. is of course not the only factor in assessing the acoustics (e.g. the amount of diffusion might have changed between the two concerts while leaving the R.T. unchanged) it is reasonably certain that it was the effect of a second hearing on the critics that made them change their minds. This is confirmed by the fact that of another eight critics who were in the Hall for the first time on 15th April, seven wanted more fullness of tone. This result was not unexpected; BAGENAL had forecast at an early stage that it would take several months for musicians used to more traditional halls to get used to the acoustics of the R.F.H.

In view of this unreliability there is little point in giving any further results of these subjective assessments, except to state that, at the final test on the 15th April, of the second class of listeners (the "specialists") who had then been four times to the Hall, one gave B as the best position, two gave C, three gave D and four expressed no preference; of the professional music critics who had then been twice to the Hall, three preferred position B, two position C, nine position D and two expressed no preference.

Although these test concerts were not useful for absolute judgments, it should be emphasised that they were invaluable for three main reasons. The first was that the removal of the absorbent areas undoubtedly caused an improvement in the acoustics. It would not have been practicable to remove them when the Hall was in use and if they had not been removed the R.T. would have been shorter than it is now: it is shown below that the R.T. should not be any shorter. At the same time it was possible to check (by using the groups of listeners) that this removal of absorbent did not give rise to any serious echoes. The second reason was that the only major fault noticed — the bad acoustics at the back of the Grand Tier — was corrected before the opening. If other and more serious faults had occurred, e.g. the sort of resonances found by JORDAN [10], these too could have been eliminated. Any such faults not corrected before the opening would have been very difficult to deal with when the Hall was in use and might have affected its reputation seriously. The third reason was that under the conditions of the test concerts it was possible to make measurements, both objective and subjective, which would have been impracticable at normal concerts.

### 3. OBJECTIVE MEASUREMENTS

#### a) Technique

Western Electric type 640 AA condenser microphones were used for most of the measurements. These were 2.5 cm in diameter and were calibrated by the National Physical Laboratory to an accuracy of  $\pm 1$  dB. The R.T.'s were measured using octave filters followed by a calibrated logarithmic level recorder [14] set at a writing speed of about 200 dB/s. The pistol used as a sound source for most of the R.T. measurements was a 0.45 inch Colt, and was fired from the front centre of the orchestra platform. Unless otherwise stated, the average value of the decay between  $-5$  and  $-35$  dB following the maximum deflection on the logarithmic recorder was taken to represent the R.T. The four microphone positions used are shown in Fig. 4. Position A was half-way between the floor and the ceiling; positions B, C and D (in the Stalls, Terrace Stalls and Grand Tier respectively) were all at ear height.

If the conditions are carefully controlled it is possible to measure R.T.'s with great relative accuracy. For example, the coefficient of variation (the standard deviation divided by the arithmetic mean) obtained from firing 101 pistol shots with the microphone in one position was found to be between 1 and 3 per cent for all octaves. However, under most conditions of measurements this accuracy can not easily be maintained (largely because of difficulties of "interpretation" of the traces) and the coefficient of variation is probably about 5 per cent for the R.T. results presented here. All values given for the R.T.'s are the mean of at least six readings, so that we can expect differences of 0.1 s between mean values to be significant (in the statistical sense if not subjectively).

To check the effect of the source of sound on the measurement of R.T., the results using (a) pistol, (b) warble-tones ( $\pm 10$  per cent about the mean frequency up to 2000 c/s and  $\pm 200$  c/s at higher frequencies) from loudspeakers and (c) an orchestra playing staccato chords were compared (Table I). (These measurements were made in the empty Hall during the test period.)

It is seen that the pistol and the orchestral chords gave the same results within the limits of experimental error; in the results to be given below for the R.T.'s during the test concerts, the values given will be for either the pistol or orchestra. The warble-tones also gave the same results except at the highest frequencies. This was due to the fact that octave bands are too wide for ranges where the R.T. is changing rapidly with respect



to frequency. The results from warble-tones can be regarded as the “true” values. Nevertheless the values obtained from octave analysis will be used throughout this part of the paper since the pistol and orchestra had to be used as sources for most of the measurements.

Table I  
Reverberation times [s] using different sources

octave [c/s]	warble tone mean frequency [c/s]	pistol	orchestra	warble- tones
75–150	120	1.91	1.91	1.90
150–300	240	2.05	2.04	2.04
300–600	480	2.14	2.08	2.10
600–1200	960	2.24	2.22	2.26
1200–2400	1900	2.18	2.11	2.19
2400–4800	3800	1.99	1.95	2.00
4800–9600	7600	1.65	1.66	1.24
6400–12800	10000	1.46	1.51	0.90

b) Reverberation time during construction  
and test concerts

The R.T. of the R.F.H. was measured at various stages during the construction (Fig. 6). For all these measurements the microphone was at position A. The first measurement was made in August 1950; the roof and structural walls were complete but the false floor which carries the seats was not installed, nor were any of the finishings. At just below ceiling height was a layer of planks laid loose on scaffolding covering the whole ceiling area. At the time of the next measurement (in October 1950) the ceiling, the wood-wool margins and the false floor had been installed; the layer of scaffolding planks just below the ceiling was still in position. Otherwise the conditions in the hall were very similar to the previous measurement. It is seen that the R.T. at 125 c/s had dropped from 5.4 to 2.9 s and at 500 c/s from 4.1 to 2.8 s. If we allow for the absorption of the wood-wool, and make a rough guess that of the other additional absorbent 80 per cent was due to the ceiling and 20 per cent was due to the false floor, we get absorption coefficients of about 0.3 for the ceiling and 0.1 for the floor at 125 c/s, and 0.1 for the ceiling and 0.05 for the floor at 500 c/s. These very approximate calculations show that the ceiling was acting as quite an efficient panel absorbent, presumably partly due to the use of vermiculite plaster described above. At the time of the next measurement, in January 1951, all the elm panels on the side walls had been installed. Some of the other finishes, e.g. the “Copenhagen” absorbent, had also been installed, but the layer of scaffolding planks below the ceiling had been removed. Most of the rock-wool was

in position on the rear and side walls ready to be covered by the leather-faced panels. The net result was that at low frequencies the R.T. was shorter but at higher frequencies (1000 c/s and upwards) the R.T. was practically unchanged. If we make another rough calculation for 125 c/s and guess that 80 per cent of the extra absorption was due to the elm panels, we get a coefficient for them of about 0.35. Allowing for the fact that the scaffolding planks had been removed, this value is close to the laboratory figure of about 0.4 [13]. The fourth curve of Fig. 6 shows the R.T. of the Hall completed except for the seats. The big increase in R.T. at mid-frequencies was presumably due to the removal of all the builder’s material that had previously been lying about in the Hall and to the covering-over of the rock-wool on the rear and side walls.

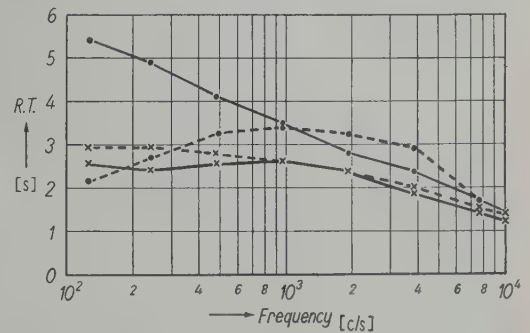


Fig. 6. Reverberation times at various stages during construction.

- August 1950
- × October 1950
- × January 1951
- February 1951

During the period of the test concerts, measurements of the R.T. were made at microphone position A (Table II).

Table II  
Reverberation times [s] at test concerts

octave band [c/s]	14/2/51		14/3/51		15/4/51	
	full	empty	full	empty	full	empty
75–150	1.8	2.1	1.8	1.9	1.5	2.0
150–300	1.8	2.7	1.8	2.3	1.6	2.0
300–600	1.7	2.9	1.7	2.3	1.6	2.0
600–1200	1.7	3.3	1.6	2.5	1.6	2.1
1200–2400	1.6	3.0	1.6	2.4	1.6	2.1
2400–4800	1.4	2.4	1.4	2.1	1.4	1.9
4800–9600	1.1	1.6	1.3	1.6	1.3	1.6
6400–12800	1.0	1.4	1.2	1.4	1.1	1.3

At the time of the first test concert on the 14th February, the auditorium was complete except for the seats, the doors and the temporary screen in front of the organ. The audience, num-



bering about 2800, were seated on the floor; the values of absorption in Sabins per person calculated from the measured R.T.'s were:

frequency [c/s]:	125	500	2000	4000
Sabins [m <sup>2</sup> ]:	0.10	0.32	0.38	0.39

As mentioned in Part 2, some absorbent areas were removed before the second test concert on 14th March 1951. These modifications were: the wood-wool margins and the wood-wool ceiling at the back of the Grand Tier were plastered over except for three small areas, and the rock-wool was removed from behind all the elm panels on the side walls. During this period about one-third of the permanent upholstered seats were installed and at the second test concert plain chairs were provided for the rest of the audience area. Unfortunately, at this concert (and at the subsequent ones) the number in the audience fluctuated throughout the period of the test; as the measurements were spread over the whole period the results are not particularly significant except to show that the changes in R.T. were small. Thus at this second test, the R.T. was practically unchanged at all frequencies up to about 5000 c/s; at higher frequencies the R.T. was rather longer. There were too many changes in the conditions for any calculations of absorption coefficients to be made.

Before the final test concert on the 15th April, some more changes were made. These were: the filling-in of the air spaces behind about half the total area of the elm panels on the side walls; the removal of the rock-wool from behind the "Copenhagen" absorbent, from behind the wood-panels on the splay walls and from underneath the orchestra platform; and the filling-in of the air spaces behind the leather cushions on the rear wall and the side walls, and of those behind the curtains behind the boxes. During the same period nearly all of the remainder of the permanent seats were installed and the carpet was laid. The net effect was that at low frequencies the R.T. was slightly shorter while at mid and high frequencies it was unchanged.

To sum up the results of the test period: the installation of the permanent upholstered seats offset the removal of the absorbent areas. The net effect was that the R.T. throughout the test period was very little changed at mid and high frequencies and was slightly shortened at the low frequencies.

### c) Reverberation times in completed hall

During the test concerts none of the audience was standing and the choir seats were unoccupied.

For normal concerts and when at least 80 per cent of the seats are sold the conditions are different. The choir seats are always occupied, either by a choir or by audience, and there are about 120 standing audience in the side-balconies, while some of the seats may be empty. This is because of the relative prices of the seats. When all the seats are sold there are usually another 150 standing at the sides and back of the Hall. Thus the R.T. of the full, completed Hall is shorter than that measured at the last of the test concerts and on which the previously published [2] figures of the R.T. were based.

The R.T. in octave bands has been measured at several concerts when the seated audience has varied between 80 and 100 per cent capacity and the choir and standing audience between 250 and 500. No significant variation (i.e. no difference as great as 0.1 s) was found in the measured R.T. over this range of audience size, and only slight differences were found between the microphone positions A, B, C and D. There were not sufficient measurements to be able to decide on the exact differences between positions and the average value for position A (corresponding to the microphone position used in other halls) has therefore been selected to give the R.T. characteristic for the full Hall (Table III and Fig. 7).

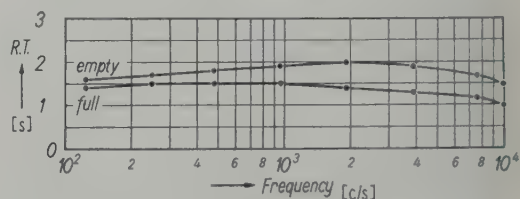


Fig. 7. Reverberation time of completed Hall (microphone at position A).

Table III  
Reverberation times [s] in completed hall

octave [c/s]	hall full position A	hall empty			
		A	B	C	D
75—150	1.4	1.6	1.7	1.6	1.6
150—300	1.5	1.7	1.9	1.7	1.7
300—600	1.5	1.8	2.0	1.9	1.8
600—1200	1.5	1.9	2.1	2.0	2.0
1200—2400	1.4	2.0	2.1	2.1	2.1
2400—4800	1.3	1.9	1.9	1.8	1.9
4800—9600	1.2	1.7	1.5	1.4	1.5
6400—12800	1.0	1.5	1.3	1.3	1.3

In the empty Hall, the variations in the R.T. between the microphone positions could be determined with more certainty. At position B the R.T. at mid and low frequencies was slightly longer as compared with position A; at positions C and D the R.T. was slightly longer at mid fre-



quencies only. At high frequencies the R.T. at B, C and D was rather shorter than at A.

The R.T. in the empty Hall at frequencies between 50 and 100 c/s was investigated in some detail both with the pistol plus one-third octave filters and with warble-tones. The decays in this range were very irregular and often inconsistent. For example, using the pistol and the one-third octave filter centred at 80 c/s, the decay at position A was very erratic; at position B the decay occasionally showed signs of a double slope, the first 25 dB corresponding to an R.T. of 1.3 s and the next 15 dB to an R.T. of 3 s; at position C the decay always showed this double slope; at position D the decay was regular over the measurable 40 dB for seven out of the twelve shots fired, but for the other five shots showed an initial decay rate for the first 10 dB corresponding to an R.T. of 0.8 s. In general, it was not possible to make any sense out of these results, but this erratic behaviour is probably due to the space between the false floor which carries the seats and the structural floor. This space is about 1 m high, and is connected to the auditorium by a large number of ventilation openings; although the floor of the space is covered with 5 cm of rock-wool, the R.T. measured inside it was 6 s at 50 c/s falling to 4 s at 125 c/s.

d) Noise levels

As mentioned above, a detailed description of the sound insulation and noise levels is to be given elsewhere, but a brief statement of the noise levels in the finished auditorium is of interest here. The overground trains were found to be completely inaudible in the auditorium, but the under-

ground trains produced a low-frequency noise which was audible for about 5 seconds for each train. At the time of writing, the sound pressure levels due to the underground trains have not been measured, but subjective measurements using a Barkhausen meter, while very approximate, showed that the noise level reached a maximum in the empty Hall of about 30 phons. At one of the test concerts, the test groups were asked to listen for this noise; out of the total of about 240 listeners, 18 were able to detect them but only, of course, when the trains coincided with a pause or a very quiet passage in the music.

The ventilation plant was audible at a very few places (e.g. behind the boxes), where the inlet or outlet grilles were close to the listeners. The noise level at these positions appeared to be about the same as the underground trains, i.e. 30 phons. Over the major part of the seating area the plant noise was not distinguishable and the total background noise was probably of the order of 20 phons.

e) Discussion of objective measurements

Certainly the most useful measurement from the practical point of view is the R.T. The measurements made in the R.F.H. during construction and during the test concerts provided a firm basis for the discussions on what alterations to make. Further, in the completed Hall it is the only well-established criterion for comparison with other halls (Fig. 8). For R.T. measurements in a full hall the orchestra is normally used as a source, and analysis into octave bands is sufficient over most of the frequency range. The use of narrower bands reduces the accuracy when, as

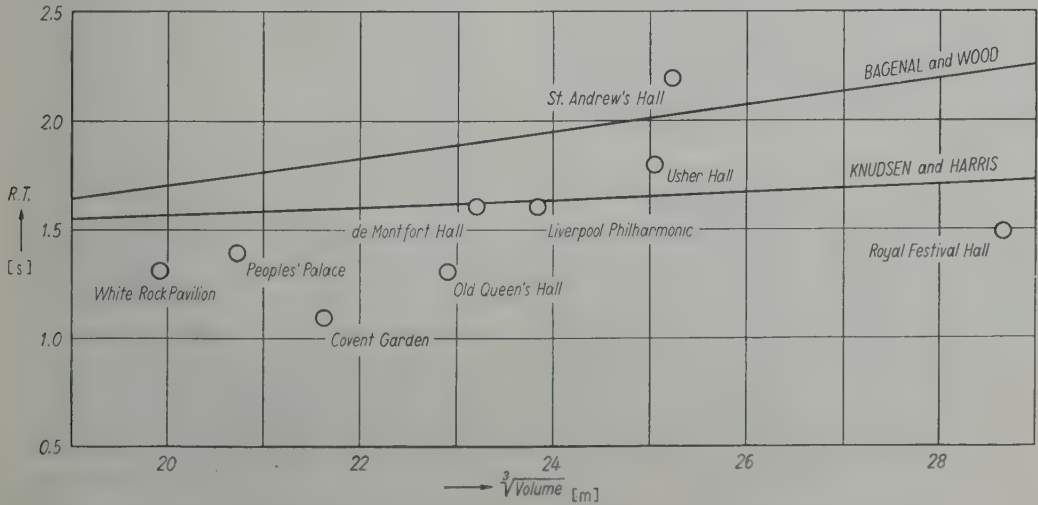


Fig. 8. Reverberation times (500 c/s) of eight good halls (full) and of Royal Festival Hall (full).



happens in practice only a limited number of measurements are possible, by increasing the spread of results in a given band due to the variations in the spectrum of the orchestral sound. At low and high frequencies however where the R.T. may be changing comparatively quickly with respect to frequency, octave-band analysis can usefully be supplemented by one-third octave analysis. In empty halls it seems logical to use a similar method of measurement, e.g. a pistol and octave analysis in preference to, say, warble-tones. In the R.F.H. no difference was found between pistol shots and warble-tones (cf. Table I) but this is not always the case. As to the desirable standard of accuracy, there seems to be little point usually in presenting results with any greater accuracy than to the nearest 0.1 s; changes in the conditions, such as the number of audience present, would nullify any greater accuracy, and it is unlikely that subjective impressions would be affected by changes smaller than 0.1 s. Of course for special purposes greater accuracy may be useful, as for the detailed examination of the variation of R.T. with position.

The absorption of the seats used in the R.F.H. had previously been measured in a reverberation chamber (volume 320 m<sup>3</sup>), three rows of ten seats each being measured with and without persons sitting in them (Fig. 9). It is not possible to compare the absolute values obtained in the reverberation chamber with measurements in the Hall itself, but the relative values i.e. the differences in absorption between the seats occupied and unoccupied should be comparable using the R.T. values for the Hall full and empty. However, little agreement was found between the relative values compared in this way; at low and mid frequencies the difference between occupied and unoccupied seats in the Hall was only about half the difference found in the reverberation chamber. Only at the higher frequencies did the values compare at all reasonably.

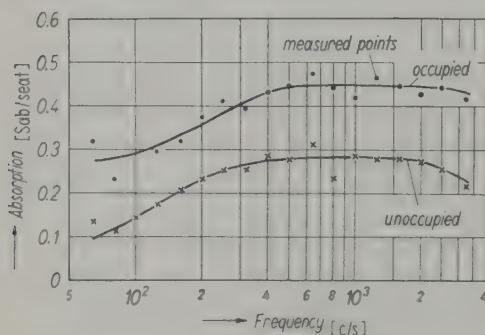


Fig. 9. Absorption per seat measured in reverberation chamber.

All objective measurements other than the R.T. are still tentative and the authors can do no more at the present stage than indicate what, in their view, are the most promising lines of development. To be of practical use, objective measurements should, in the long-term, be capable of fulfilling three conditions. First, it should be possible to state the results in a quantitative metrical form. Secondly, it should be possible to correlate the objective measurements with subjective impressions either as being typical of a hall as a whole or as relating to particular positions in a given hall. This does not necessarily mean that one particular type of objective measurement need be directly related to one particular subjective quality. If a measurement is to refer to a particular position, its value should not change too quickly with position. In other words, a measurement which gives one value at a given seat is of little use if its value is quite different only two or three seats away, because obviously a listener would hear no difference between the two positions. Thirdly, it should be possible, ideally, to make the measurements in full halls, but as this is unlikely, the type of measurement should be such that the results are not too dependent on the full or empty state of the hall. This difficulty is greatest in the older halls which often have plain wooden seats. For example, the R.T. at 500 c/s in St. Andrew's Hall, Glasgow, and in Usher Hall, Edinburgh, is 50 per cent longer when these halls are empty than when they are full; in the more modern halls with upholstered seats this difference is less; in the R.F.H. it is 20 per cent.

The authors have made a large number of measurements of various types in the R.F.H. and in other concert-halls, but most of them do not appear to be particularly useful in such large rooms although they are no doubt useful in smaller rooms, e.g. studios. To mention only two types of measurement, the frequency irregularity [15], [16] and the distribution of R.T.'s with position [17] have been measured in the R.F.H. and in other halls. The maximum frequency irregularity in rooms of this size occurs at very low frequencies, between 15 and 60 c/s; at higher frequencies we are on the tail of the curve and can expect the measured values to be much the same independent of the shape of the rooms. Thus in two other halls of comparable size, St. Andrew's Hall, Glasgow and Usher Hall, Edinburgh, the authors have found [3] similar values to those found in the R.F.H. i.e. between 2 and 4 dB per c/s. The distribution of R.T.'s in the R.F.H. was found to be normal, but in other halls the distribution



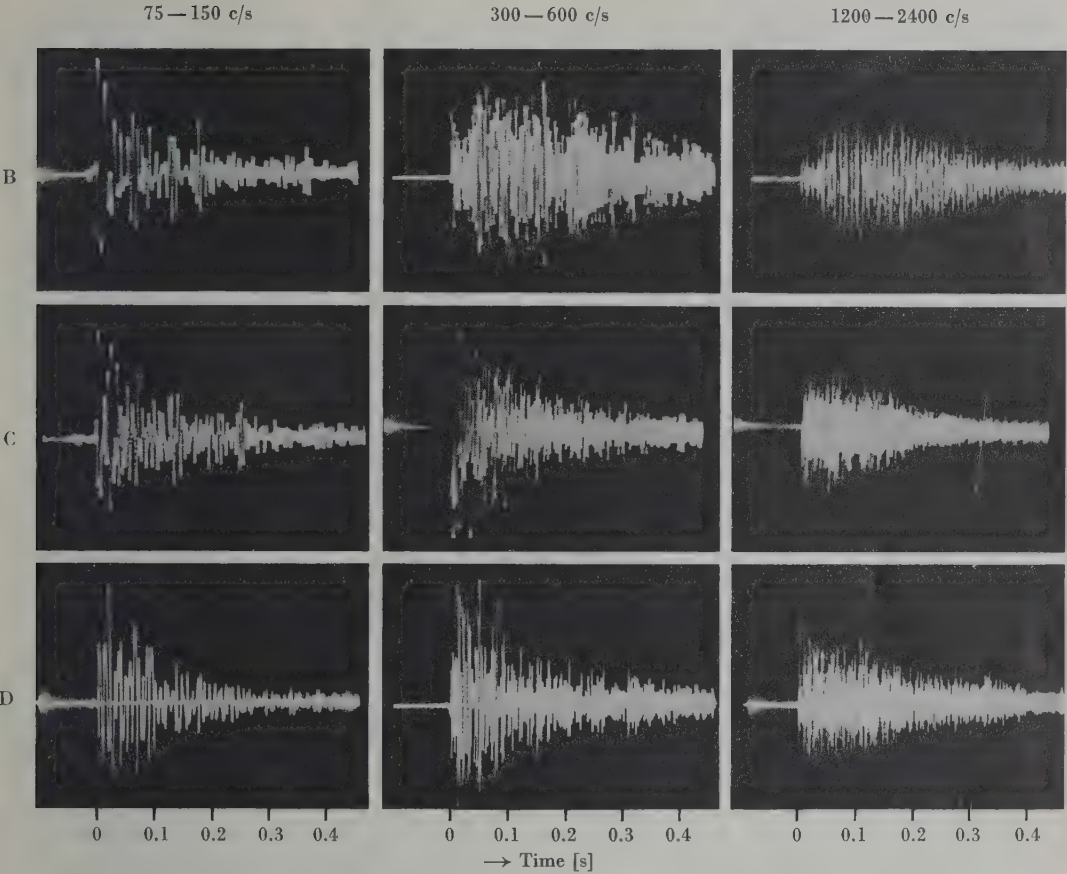


Fig. 10. Transient responses at positions B, C and D at the last test concert.

has been found to be skew on some occasions but not on others.

As we are concerned here with practical problems, it appears that most progress can be expected by working in terms of geometric acoustics. That is to say, we should examine at a given point in a hall the variation with time, direction and frequency of the pressure received when an impulsive or a continuous sound is emitted from the source. There would be a hope of correlating such measurements with subjective impressions, perhaps not directly but through intermediate laboratory experiments. An excellent example of this method has been the work of HAAS [7] supplemented by the work of BOLT and DOAK [18]. HAAS established the effect of single “echoes” on the subjective hearing of speech, and BOLT and DOAK showed that the results could be applied to speech in rooms. A similar technique for music would be more complicated, but some definitive results could be expected.

The complementary measurements needed in a concert-hall would require first a non-directional

source for impulsive and steady sounds. For the impulsive sounds either pulses of tone from a loud-speaker or explosive sources such as a pistol or an electric spark could be used. If a loud-speaker source is used it must be made non-directional, e.g. by the use of several loud-speakers mounted on a spherical or hemi-spherical baffle, and the pulses must be very short. Certainly a pulse length of 25 ms is too long; measurements made in the R.F.H. using this pulse length showed very large variations in the received signal when the microphone was moved three seats and thus did not satisfy the second criterion for objective measurements. Pulses of only 2 to 15 ms have been shown [18], [19] to give better results but with such short pulses the transient response of the loud-speaker must be allowed for, and it is difficult to put sufficient low-frequency energy into the room. An explosive source is better in these respects [20]; using the 0.45 pistol in the R.F.H. measurements were possible over most of the frequency range and the received signal varied only slowly with position. Fig. 10



shows the pressures recorded on an omni-directional microphone at the three positions B, C and D when the 0.45 pistol was fired from the front centre of the platform at the last test concert. (It should be noted that the amplitude scale is linear and that the absolute amplitudes for the various photographs are not comparable.) For our present state of knowledge these photographs are too detailed, and an attempt has been made to "smooth" them by taking the mean rectified pressure for successive 20 ms bands and plotting the results on a logarithmic amplitude scale referred to the mean pressure in the first 20 ms band (Fig. 11). The outstanding feature of these

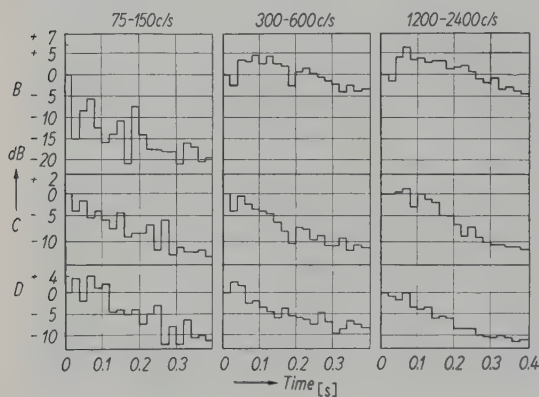


Fig. 11. Transient responses at positions B, C and D averaged over 20 ms intervals.

results is that at position B (in the Stalls) it is some 200 ms before the pressure level starts to decay. This is a reasonable result because of the reflections arriving from the canopy and the organ screen. However, this technique requires further development; rather different results are obtained from a less intense source and it is possible that there may be some non-linearity in the behaviour of the various surfaces. Further, the pressure per octave-band from a pistol shot in-

creases by about 10 dB per octave [20], thus biasing the octave-band results in Figs. 10 and 11; it might have been better to insert an equalising network before the octave analysis.

There was a slight hope that, to overcome the difficulty of making measurements in full halls, a staccato chord could be used as the source for these transient responses. Fig. 12 shows the results at position C for the same test concert using a chord from bar 13 of the overture "Coriolanus". It is seen that the duration of the chord was far too long for any such measurements.

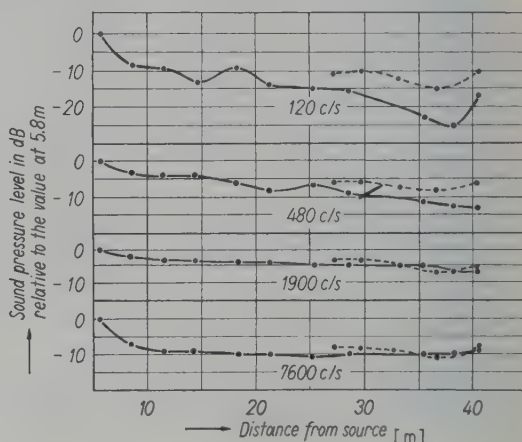


Fig. 13. Steady-state sound pressure levels.

● — Stalls Level  
● - - - Grand Tier Level

The transient measurements might well be supplemented by steady-state measurements, if only as an indication of the relative pressure levels throughout a hall. Fig. 13 shows the sound pressure levels in the R. F. H. using a loud-speaker fed with warble-tones at the centre of the orchestra platform. The pressures were measured along the centre-line of the Hall; the pressures at three closely-spaced microphone positions have

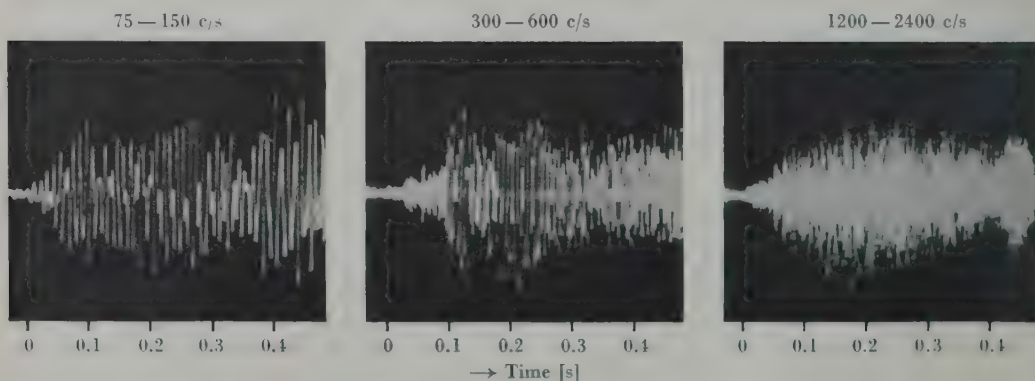


Fig. 12. Transient responses from chord from "Coriolanus".



been averaged to give the levels at each point. It is seen that at 120 c/s the pressures along the Stalls level fall off quicker than the inverse-square law which indicates, surprisingly, that the reverberant sound is negligible and that there is strong absorption by the seats. Along the Grand Tier the levels correspond roughly to the inverse-square law. At 480 c/s the fall off is close to the inverse-square law along the Stalls, while the pressures in the Grand Tier are again rather greater. At the two higher frequencies the reverberant sound appears to have much more effect.

If these measurements with an omni-directional microphone were to be extended using a directional microphone, we could expect to obtain results which would define completely the behaviour at given points in the room. This discussion has only been concerned with tentative methods, but it is hoped that enough has been said to indicate the most promising lines of development.

## 4. SUBJECTIVE ASSESSMENTS

### a) Press comments

A fairly comprehensive review of the comments in the national press (not the musical press) on the acoustics of the R. F. H. has been made throughout the first eighteen months since the Hall's opening (omitting comments on the test concerts). The terms used in describing the acoustics have been: clarity (twenty times); brilliant (five times); beautiful, blend, definition, resonant (all four times each); alive, balanced, exhilarating, frightening, perfect, ruthless, shattering, subtle, superb, truthful, warm (all twice each); admirable, astonishing, charitable, charming, Chaucerian, cold, consolidated, dazzling, deplorable, eerie, exalting, exquisite, frank, full, glorious, hard, ice-clear, inspiring, intimate, lovely, magnificent, magnified, mellow, merciless, muddy, overbearing, ravishing, responsive, revealing, rich, ruinous, sharp, shimmering, shrill, sickening, sonorous, stunning, temperamental, toneless, touchy, tremendous, unrelenting, wonderful (all once each). (If it is thought that this list of 60 terms is overlong, it should be compared with the 140 terms [21] used in sound recording and reproduction.)

Ignoring the more esoteric descriptions, these press comments may be interpreted in terms of the requirements set out in Part I. There were about 100 comments, and the numbers of comments on the particular acoustical qualities are shown in Table IV.

Table IV  
Press comments in first eighteen months

quality	number of comments	
	favourable	unfavourable
Definition or clarity	24	3
fullness or resonance or singing tone	15	10
blend	8	3
balance	15	7
echoes	2 comments on absence of echoes	

In addition, there were 20 favourable and 11 unfavourable comments on the sense of climax for loud passages, 8 favourable and 4 unfavourable comments on the string tone, 4 favourable and 1 unfavourable comments on the brilliance, and 7 comments that the acoustics were particularly good for small bodies of players.

### b) Stokowski concert

Dr. LEOPOLD STOKOWSKI conducted a concert in the R. F. H. on 9th June, 1951. Following discussions with the acoustic consultants, Dr. STOKOWSKI arranged the orchestra with all the strings on one side so that they were all more or less facing the audience (Fig. 14). The purpose of this arrangement was to see if it had any effect on the string tone. A letter was sent to all music critics who had assisted at the test concerts asking them to give their opinions of this concert and seven replies were received. Of these seven, one was seated on the right-hand side of the second row of the stalls, and he said that even in this position the resonance and tone were far better than he had heard in any other hall. He also said that the balance was much better than he had ever found in similar positions in other halls. The other six critics were all at about the middle of the Hall. Five of them commented that the string tone was better than they had ever heard in this Hall, although three out of the five qualified this remark by stating that it was probably as much due to the excellence of the conducting as to the orchestral lay-out. Three out of the six said that the balance was excellent, one said the balance was fair and one said the balance was poor in the Beethoven and Bach works in the programme but good in the Stravinsky work. In general, the comments were very favourable. It should be noted that at this concert there were 118 players in the orchestra, that is an orchestra of the size for which the Hall was designed compared with the more common size of 80 to 90 players.

### c) Foreign scientists

A concert in the R. F. H. on 16th September, 1951 was attended by 18 foreign scientists all of whom were engaged in acoustical research. They were: Mr. P. ARNI, Finland; Professor L. L. BERANEK, U.S.A.; Dr. R. BERG, Norway; Professor R. H. BOLT, U.S.A.; Professor F. BRUCKMAYER, Austria; Professor F. CANAC, France; Dr. L. CREMER, Germany; Ir. J. VAN DEN ELJK, Netherlands; Professor W. FURRER, Switzerland; Dr. J. J. GELUK, Netherlands; Dr. C. M. HARRIS, U.S.A.; Mr. F. INGERSLEV, Denmark; Professor C. W. KOSTEN, Netherlands; Mr. P. A. DE LANGE, Netherlands; Professor E. MEYER, Germany; Mr. A. MOLES, France; Dr. H. OBERST, Germany; and Professor A. C. RAES, Belgium. They were divided into three groups and sat successively in different positions in the Hall. These positions were: Front Stalls (seventh row, some in the centre and some towards the left), Terrace Stalls (seventh row, in the centre) and Grand Tier (seventh row, in the centre). They were given a questionnaire and their answers were as follows:

1. Four preferred the Front Stalls, nine the Terrace Stalls, three the Grand Tier and two expressed no preference.

2. One wanted more definition, six more fullness and eleven no change.

3. Three knew better halls, and they were: (i) Concertgebouw, Amsterdam, because of more reflections from a distance but which were not perceptible as discrete echoes; (ii) Concertgebouw, Amsterdam, because of more fullness; and (iii) three concert-halls in Basle, Zurich (Tonhalle) and Berne (Casino), because they had a much closer contact between the orchestra and audience and because the loudness was better than in the R. F. H. Two others gave concert-halls which were better in some respect but not on





Fig. 14. Dr. Leopold Stokowski conducting the BBC Symphony Orchestra on the 9th June, 1951.

the whole; e.g. the Musikverein's Hall in Vienna was mentioned as having greater fullness. Nine stated definitely that they did not know any better hall, and four did not commit themselves.

The fourth question was: "Apart from your own preference, if you were asked by the musicians to provide (a) more definition or (b) more fullness of tone, how would you do it?"

(This question was badly worded, as "musicians" was not defined and was queried in a few replies as referring to the players or the listeners. However most replies seemed to understand the question — as was intended — as referring to musician listeners.) To increase the definition, six suggested more reflecting surfaces closer to the orchestra, and three said lower the canopy. One said raise the height of the platform and two said shorten the R.T. To provide more fullness, seven said increase the R.T. (of which seven, five particularly mentioned the low-frequency R.T.); one said more diffusion; one said reduce and one said increase the reflecting surfaces close to the orchestra.

From the above answers and from the general comments made by these listeners it is possible to divide their opinions into two broad classes. Thus thirteen of the listeners would put this Hall in the "excellent to very good" class (BERANEK, BERG, BOLT, BRUCKMAYER, CANAC, CREMER, VAN DEN ELJK, HARRIS, INGERSLEV, MEYER, MOLES, OBERST and RAES), and the other five in the "good" class (ARNI, FURRER, GELUK, KOSTEN and DE LANGE).

#### d) Acoustic Group Meeting

The Acoustics Group of the Physical Society held a meeting [22] on the 23rd November, 1951, to discuss the acoustics of the R.F.H. Contributions to the discussion were made by conductors (Dr. Stokowski had previously recorded his views on the acoustics), music critics, orchestra managers, performers and musical educationalists. Most of the speakers had been previously invited by the Acoustics Group to contribute, largely on the grounds of their known interest in the subject, and the contributors can not be taken as a scientifically selected cross-section of the musical

world. Nevertheless, they were probably more fully representative of musical opinion than the comments in the general press, and this meeting is certainly the most authoritative musical review of the acoustics that has as yet taken place.

It is convenient to divide the contributors into two classes: performers and listeners. Of the performers, the conductors (BEECHAM, BLECH, BOULT, KRIPS, SARGENT, STOKOWSKI) were on the whole very pleased with the acoustics and three of them (KRIPS, SARGENT, STOKOWSKI) said that it was the best hall they knew. However, all except KRIPS qualified their praise by a request for a little more "resonance". Two other performers (Miss JOAN HAMMOND and Mr. DENIS MATTHEWS) also were very pleased with the acoustics, but again one (MATTHEWS) wanted a little more resonance. Another

performer (HEIFETZ) said, by proxy, that it was the finest hall in the world.

The three chairmen or secretaries of the main London orchestras (Royal Philharmonic, London Philharmonic and London Symphony) can, from their remarks, be classified as listeners. One made three points: that the smaller the number of performers the better it sounded; that there was a weakness under the Grand Tier but that otherwise it was good; and that there was a cross-echo at the front from trumpets. The other two said that their orchestras were coming more and more to like playing in the R.F.H., but both stressed the need for more resonance for the listeners and one said that the players needed a little more help in hearing each other. Of the nine other listener contributors (three of them professional music critics) five wanted more fullness, and two did not; two complained that the middle sections of the orchestra were sometimes lost, but one did not agree; two suggested that more orchestral lay-outs should be tried to overcome some of the difficulties.

Throughout the whole discussion there was general agreement that the definition and clarity in the R.F.H. were outstandingly good, and there were several comments that this has led to an improvement in orchestral performance.

#### e) Casual observations

From casual observations made by the authors, three points are worth mentioning. The first is that under normal concert conditions it is possible to hear a change in the quality of the orchestral sound as one moves to the extreme back of the Terrace Stalls, i.e. under the Grand Tier. This "under-balcony" effect is, of course, quite common and is not in this case very great. However, on one occasion an orchestra was playing on a flat platform specially erected for ballet performances, and which was 1.5 m high compared with the 23 cm height of the front of the usual platform. Under this condition it was not possible to hear any change in the sound between the back and the front of the Terrace Stalls, although it should be mentioned that all these seats were empty.



The second point is that in the boxes and the side stalls it is possible to hear slight high-frequency echoes, particularly from the brass. These are presumably due to the removal of the absorbents from behind the "Copenhagen" strips and to the plastering-over of most of the wood-wool margins.

The third point is the unusual loudness of the sound at the back of the Grand Tier. This is particularly noticeable with solo instruments or voices, so much so that there is a conflict between sight and sound. The performer from this distance (41 m) looks, of course, quite small yet the sound is "unnaturally" loud.

#### f) Discussion of subjective assessments

The opinions expressed about the acoustics of the R.F.H. have been given in some detail because the science has now reached the stage where we can attempt to obtain in the design — if not to measure — definite musical qualities, as distinct from the broad classifications of good or bad acoustics. We can not hope to get what might be called absolute opinions; in other words we can not get opinions under controlled conditions, such as comparing directly slightly different acoustical conditions. This however is not a serious criticism of the opinions presented here. The fact is that these opinions are what people have said and what they believe; this definition of the validity of the opinions is sufficient for the present writers.

One difficulty with subjective assessments is the use by musicians of a large number of terms, and to bring order into the problem it has been necessary to translate some of their opinions into our own terms. It does appear however that there is not much difference between many of these terms, certainly not enough to be of any consequence when dealing with design problems.

The general opinion about the R.F.H. is that its acoustics are very good, several distinguished individuals going so far as to say that it is the best of its size in the world. "Of its size" is an interesting qualification but one which we need not worry about here; concert-halls, in this country at least, have to be of this size if they are to be at all economic. Dealing with the acoustic qualities in detail, it is obvious that the definition in this Hall is exceptionally good. It is also established that there are no echoes nor intruding noise sufficient to call for comment. There is not such universal agreement on the other qualities, although there have been more favourable than unfavourable comments about all the qualities. The blend has been criticised on some occasions but this is not entirely an acoustical phenomenon; on occasions one orchestra has been criticised for lack of blend and, a few days later and by the same critic, another orchestra has been praised for the excellent blending. This remark also applies to a certain extent to balance; the platform has been designed to give all instruments as equal a chance as possible and, in the authors' opinion, it is now the responsibility of the conductors to achieve good balance. It would be interesting to see some more experiments made similar to the Stokowski concert.

The most important criticisms have been concerned with fullness of tone and, what is presumably connected with it, the sense of climax at loud passages, particularly with the extreme romantic composers such as Wagner. Most, not all, of the musicians want more fullness but only a little more. On the other hand, of the 18 scientists six wanted more fullness and one more definition but 11 wanted no change. It should be noted that there appears to be no lack of fullness for the quieter and more classical pieces of music, in fact there have been several comments that the Hall is very satisfactory for small bodies of players and several chamber music concerts have been given in it with complete success.

## 5. CONCLUSIONS

The main conclusions that the authors would draw from the above objective and subjective results are most usefully discussed in terms of what they would alter if they had again to advise on the acoustical design of the Hall. On all major points they would not change the design. The R.F.H. is a good hall acoustically with no serious faults; the rectangular plan is still favoured because of the smaller risk of echoes; the good sound-insulation may be helping the definition, has made possible the use of the Hall for chamber-music and, by enabling orchestras to play very quietly, has increased the dynamic range possible; the canopy and the raking of the seats have produced excellent definition and uniform conditions.

The only criticisms which have been at all serious are those concerning lack of fullness. The authors hold to their original view that this lack would be overcome by a longer R.T.; the value of 1.5 s at 500 c/s is 0.2 s below the KNUDSEN and HARRIS optimum (Fig. 8). It may be that an increase of 0.2 s would be sufficient, but a greater increase might be better, although the upper limit is indicated by the fact that when listening to rehearsals during the test period (the R.T. was about 2.3 s) the definition was appreciably worse. In any new design it would be desirable to make every effort to get the R.T. at mid-frequencies as long as possible; if it were found that it was too long it would be a simple matter to shorten it, e.g. by introducing carpets or by perforating wood panels. The Appendix shows that over half the total absorption at mid-frequencies in the full Hall is due to the seats and the audience, which indicates that an increase in the volume per seat would be the most important method for lengthening the R.T. It is still thought essential to ensure that the R.T. at low frequencies is not too long; this would be a major fault as compared with the minor defect of a too short R.T. However in the R.F.H. as it is at present any increase in the R.T. at mid-frequencies should be supplemented by a corresponding increase in low frequencies. It might be that a greater increase at low frequencies, or even an increase only at low frequencies, would be the most effective way of increasing the fullness. The criticisms of lack of fullness have applied only to the louder passages of romantic and choral music, although there have been comparatively few concerts with large choirs. This lack does not always occur; it may be simply that, for this class of music, most orchestras are a little too small for a hall of this size, or it may be that the absorption of some of the surfaces varies with intensity.

On minor points, the authors would not change the design of the canopy except that it might be better to obtain more blending by a general "closing-up" of all the surfaces round the orchestra; this could not be done in the R.F.H. because of the very large organ opening required. The organ is always a difficulty (acoustically) in a concert-hall and it is debateable how far the orchestral and choral conditions should be sacrificed in order to help the organ. The canopy in the R.F.H. has, for the sake of the organ, been made higher than the authors would have wished, and although this does not appear to have hindered the definition it has probably detracted from the blend.

The danger of the screening of the middle instruments by the front instruments was probably exaggerated; it occurs mainly in halls with flat floors and it might have been better in the R.F.H. to have a higher platform front while still keeping the platform rake. Any screening would only have affected the front two or three rows, and several rows at the back of the Terrace Stalls would have been helped. Also, it would have been better to keep to the calculated rake; at the back of the Terrace Stalls the total difference between the calculated rake and the straight line adopted was about 75 cm, but the greater height, small as it is, might have helped considerably. Apart from this slight weakness at the back of the Terrace Stalls, the uniformity of the acoustics is good. This is particularly so at the back of the Grand Tier and it would have been possible to go further back here with little ill-effect acoustically, although in a sense, the limit on visual grounds has just about been reached.

It should be emphasised again that this paper has been concerned with the practical aspects of concert-hall design. A large number of factors enter into a full discussion of concert-hall acoustics, factors such as new halls affecting opinions, the change of music with time, the reactions of the ordinary public, and economic considerations. This paper represents the views of the authors, based largely on their experience with the R.F.H. but also influenced by two other new concert-halls (Colston Hall, Bristol, and Free Trade Hall, Manchester) with which they have been connected. For those who disagree with these views they would end with another quotation from CHAUCER:

*"And who so sayth of trouthe I varye, Bid hym proven the contrarye."*

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The authors wish to record the pleasure it has given them to work with Mr. BAGENAL and with

the L.C.C. architects and staff. It will be obvious from this paper that the acoustic consultants enjoyed an extremely close collaboration with the architects. This collaboration began at the earliest stages and continued in detail throughout the period of construction and testing up to the present time, when modifications are still under consideration. The willingness of the architects to meet the numerous acoustical requirements has made the work of the consultants a pleasure and, of course, has contributed greatly to the success of the Hall.

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Appendix

Calculation of absorption (Based on reverberation time measured in completed hall)

local	item	material	area [m <sup>2</sup> ]	remarks	125 c/s		500 c/s		2000 c/s		4000 c/s	
					$\alpha$	Sabins	$\alpha$	Sabins	$\alpha$	Sabins	$\alpha$	Sabins
Side walls	{ main panelling box panelling podium walls promenade back box fronts box sides box openings main doors promenade balustrade	elm panels	535		0.2	107	0.15	80	0.1	53.5	0.1	53.5
		ribbed panels	115		0.3	34	0.2	22.5	0.15	17.3	0.1	17.3
		“(openhagen, (absorbent)	77		0.3	24	0.1	19.5	0.1	19.5	0.1	19.5
		“(openhagen, (plain)	45		0.15	10	0.15	48.5	0.15	21.5	0.1	14
Platform walls	{ plywood organ dado organ front slit grille choir balustrade	leather panels	139		0.5	69.5	0.33	45	0.15	23	0.1	14
		fibrous plaster	111		0.3	33.5	0.1	11	0.04	4.5	0.04	4.5
		plaster on solid	167		0.9	16.5	0.06	10	0.04	6.5	0.04	6.5
		plaster on wood wool	141		0.9	127	0.9	127	0.9	127	0.95	134
Hear wall	{ wall under balcony fricze above balcony balcony front and balustrade	ribbed panels	102		0.2	41	0.3	30.5	0.1	10	0.1	10
		ply panels	33		0.4	6.5	0.15	5	0.1	3.5	0.1	3.5
		ply panels	147		0.4	59	0.2	29.5	0.15	22	0.1	15
		“(Matchboard”	56		0.3	17	0.2	11	0.15	8.5	0.1	5.5
Floors	{ platform and choir (incl. risers) floor reflector main seating areas (incl. risers) gangways (incl. risers) cross gangway promenades corridor promenades boxes	ply panel (temporary)	37		0.3	36.5	0.15	18.5	0.15	5.5	0.1	3.5
		ply panels	122		0.5	3.5	0.4	3	0.4	3	0.4	3
		leather panels	19		0.3	5.5	0.15	3	0.1	2	0.1	2
		leather panels	95		0.5	47.5	0.35	33	0.2	19	0.1	9.5
Ceilings	{ choir ceiling main ceiling ceiling margin ceiling under balcony promenade ceiling box soffits canopy reflector air	leather panels	77		0.5	38.5	0.35	27	0.2	15.5	0.1	7.5
		plaster on wood wool	23		0.4	9	0.3	7	0.1	2.5	0.1	2.5
		ribbed panels, etc.	93		0.3	28	0.2	18.5	0.15	14	0.1	9.5
		wood boards	390		0.4	125	0.25	58.5	0.15	23.5	0.1	8
Seats	{ upholstered seats orchestra seats (wooden) choir seats (cushions) total absorption — Hall empty R.T. — Hall empty — measured (seconds)	slate	48		0.01	0.5	0.01	0.5	0.02	1	0.02	1
		cork on solid	1384		0.1	110.5	0.1	83.5	0.1	55.5	0.1	27.5
		wood boards	49		0.15	74	0.1	49.5	0.1	49.5	0.1	49.5
		carpet	130		0.2	21	0.2	13.5	0.5	33.5	0.85	57
Audience	{ in upholstered seats in orchestra seats with instruments in choir seats standing total absorption — Hall full R.T. — Hall full measured (seconds)	wood boards	69		0.2	21	0.2	13.5	0.5	26	0.85	57
		wood boards	111		0.15	10.5	0.1	7	0.1	7	0.1	2
		as above			0.1	9	0.1	6.5	0.1	4.5	0.1	2
		plaster on wood wool	107		0.4	43	0.3	32	0.1	10.5	0.1	10.5
Seats	{ upholstered seats orchestra seats (wooden) choir seats (cushions) total absorption — Hall empty R.T. — Hall empty — measured (seconds)	5 cm fibrous plaster	1328		0.35	465	0.2	265.5	0.1	133	0.04	53
		wood wool	153		0.4	61	0.3	46	0.1	15.5	0.1	15.5
		plaster on solid	510		0.05	25.5	0.04	20.5	0.04	20.5	0.04	20.5
		plaster on solid	93		0.03	3	0.03	3	0.04	3.5	0.04	3.5
Seats	{ upholstered seats orchestra seats (wooden) choir seats (cushions) total absorption — Hall empty R.T. — Hall empty — measured (seconds)	plaster on solid	158		0.03	4.5	0.03	4.5	0.04	6.5	0.04	6.5
		5 cm wood, polished	223		0.1	22.5	0.05	11	0.04	9	0.04	9
		air	22000 m <sup>3</sup>		—	—	—	—	0.01	220	0.027	593
		upholstered seats	2750		0.18	495	0.28	770	0.27	741	0.2	550
Seats	{ upholstered seats orchestra seats (wooden) choir seats (cushions) total absorption — Hall empty R.T. — Hall empty — measured (seconds)	125		0.01	1	0.01	1	1	0.05	6	0.07	9
		250		0.02	5	0.05	12.5	12.5	0.14	35	0.19	47.5
					2204		1921	1773		1820		1820
					1.6		1.8	2.0		1.9		1.9
Audience	{ in upholstered seats in orchestra seats with instruments in choir seats standing total absorption — Hall full R.T. — Hall full measured (seconds)	192		0.07	192	0.05	137	137	0.14	385	0.23	632
		46		0.37	46	1.1	137	163	0.13	163	1.1	137
		125		0.16	125	40	0.44	110	0.37	92	0.28	70
		250		0.23	64	64	0.47	132	0.56	157	0.46	129
Audience	{ in upholstered seats in orchestra seats with instruments in choir seats standing total absorption — Hall full R.T. — Hall full measured (seconds)	2546		2437	2546	2437	2570	2788		2788		2788
		1.4		1.5	1.4		1.5	1.4		1.4		1.3

# ÉTUDE THÉORIQUE DE MOUVEMENTS VIBRATOIRES AVEC OBSTACLES ET DISCONTINUITÉS

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## Sommaire

Des mouvements vibratoires spéciaux avec obstacles ou discontinuités diverses sont analysables par poussières et capsules manométriques et susceptibles de représentations mathématiques convenables.

Ce sont d'abord des phénomènes de circulation non périodiques et des phénomènes tourbillonnaires, auxquels on peut joindre les rides de Kundt. Les lignes de courant s'obtiennent à partir de potentiels complexes et de représentations conformes dans un espace à deux dimensions.

L'étude d'un branchement (tuyau en Y) montre davantage encore la nécessité de faire appel à un certain nombre d'hypothèses, telles que les réflexions successives et l'amortissement des ondes sonores, moyennant lesquelles les résultats expérimentaux sont bien représentés.

## Zusammenfassung

Schwingungsbewegungen in der Umgebung von Hindernissen und Diskontinuitäten lassen sich mit Hilfe von Staubteilchen und Drucksonden ausmessen und sind der mathematischen Darstellung zugänglich. Dies gilt zunächst für nichtperiodische Zirkulations- und Wirbelerscheinungen, zu denen man die KUNDTSchen Staubfiguren rechnen kann. Die Stromlinien erhält man durch Anwendung von komplexen Potentialen und konformen Abbildungen im zweidimensionalen Raum.

## Summary

Special types of vibratory movement with obstacles or discontinuities can be analysed by the powder method or by manometric capsules and are susceptible to mathematical representation.

Of this type are non-periodic circulations and vortex phenomena, to which may be added KUNDT's striations. The stream lines can be derived from complex potentials and conformal representation in a two-dimensional space.

The study of a junction (Y tube) shows also the necessity of making hypotheses concerning the successive reflections and attenuation of the sound waves, having regard to which the experimental results can be well satisfied.

## 1. Introduction

### Matériel

Les expériences suivantes ont été réalisées avec un tuyau en laiton, d'épaisseur 1 mm, de diamètre variable suivant la fréquence utilisée: 4 cm pour  $N=100$  c/s, 3 cm pour  $N=300$  c/s et au delà. Ce tuyau est alimenté, à l'une de ses extrémités, par la plaque d'un téléphone dépolarisé, donnant une fréquence double de celle du courant qui le traverse.

Ce courant est celui du secteur ( $N=2 \times 50$  c/s) ou celui d'un hétérodyne à basse fréquence convenablement amplifié. Dans ce dernier cas, la fréquence est contrôlée au moyen de l'oscillographe cathodique, par comparaison avec celle du secteur. Cette dernière peut être considérée comme constante à moins de 2 % près. L'intensité du courant (de quelques mA à 200 mA) est réglée par transformateur, potentiomètre, rhéostat, suivant les cas, et mesurée par un milliampèremètre.

L'étanchéité du système, lorsque le tuyau est fermé, est vérifiée par le gaz d'éclairage que l'on chasse ensuite par un courant d'air.

### Méthodes de mesure

a) *Amplitudes.* Des grains d'amidon (de quelques microns) reproduisent fidèlement le mouvement de l'air dans lequel ils sont en suspension, pour l'amplitude et la phase, jusqu'à des fréquences de 1500 c/s. Lorsque le tuyau vibre, ils se présentent sous forme de bâtonnets dont la longueur est le double de l'amplitude. Cette longueur est mesurée au moyen d'un ultra-microscope à long foyer, la distance focale étant de l'ordre de grandeur du centimètre, soit par observation directe avec un oculaire micrométrique, soit par photographie, le temps de pose étant toujours légèrement supérieur à la période du mouvement vibratoire. Les bâtonnets peuvent atteindre 1 mm; le plus souvent, ils ne dépassent guère le dixième de cette valeur. Leur épaisseur est absolument négligeable.



b) *Phases.* Aux points convenables, sont branchés des conduits étroits (2 à 3 mm de diamètre), reliés à deux capsules manométriques. Ces dernières actionnent de façon très sensible deux miroirs dont les axes de rotation sont perpendiculaires. Un point lumineux, vu par réflexion sur les deux miroirs, se présente sous forme d'une ellipse de Lissajous, donnant les différences de phases. La longueur des conduites reliant les capsules au tuyau est choisie de manière à ne pas modifier l'état vibratoire de ce dernier.

Dans certains cas, les grains d'amidon décrivent non plus des bâtonnets, mais des ellipses qui peuvent donner directement la différence de phase entre les deux mouvements dont elles sont la résultante. Le sens de circulation du grain sur sa trajectoire est déterminé par un stroboscope à lame vibrante.

La précision des mesures est de l'ordre de  $1/50$ , ce que j'estime suffisant, la théorie élémentaire des tuyaux sonores ne permettant pas d'aller plus loin.

2. Obstacles au ventre d'un tuyau sonore

Circulations, potentiel complexe correspondant

Le tuyau utilisé est fermé; il est réglé pour donner le fondamental à la fréquence 100 c/s; par suite des corrections aux extrémités, sa longueur (160 cm environ) est légèrement inférieure à une demi-longueur d'onde.

Le problème peut être considéré dans deux dimensions:  $Ox$ , axe du tuyau,  $Oy$ , perpendiculaire à cet axe et à la direction d'observation. Les obstacles seront cylindriques, les génératrices étant perpendiculaires à  $Ox$  et  $Oy$ ; ils seront assez petits pour ne pas modifier sensiblement l'état vibratoire du tuyau.

Les poussières apparaissent sous forme de bâtonnets parallèles à  $Ox$  loin de l'obstacle, ou sous forme d'ellipses dans son voisinage immédiat. Ces ellipses et bâtonnets, par leur déplacement, mettent en évidence une circulation indiquant l'existence de plusieurs centres tourbillonnaires. De plus, certaines poussières décrivent des ellipses fixes, que j'appelle «stationnaires», dont le grand axe est approximativement égal à la longueur des bâtonnets (double amplitude du mouvement vibratoire) et dont l'un des foyers coïncide avec le centre tourbillonnaire.



Fig. 1. Ellipses stationnaires, obstacle cylindrique circulaire. Les flèches indiquent le sens de parcours de l'ellipse par la poussière.

Je me suis proposé de rechercher des expressions mathématiques rendant compte de ces circulations au moyen de potentiels complexes, permettant le tracé des lignes de courant correspondantes.

Cylindre circulaire (Fig. 1)

Le potentiel complexe:

$$\psi(z) = -V_0 \left( z + \frac{R^2}{z} \right)$$

correspondant à un écoulement avec obstacle cylindrique de rayon  $R$  ne donne pas de tourbillons.

Considérons le potentiel:

$$\Phi(z) = iM \log \frac{(z-A)(z-C)}{(z-B)(z-D)} \tag{1}$$

dans lequel:  $M$  est une constante réelle,

$$z = x + iy = \rho (\cos \Theta + i \sin \Theta),$$

$$A = r (\cos \varphi + i \sin \varphi).$$

$B, C, D$  sont symétriques de  $A$  par rapport aux axes de coordonnées et se suivent dans cet ordre dans le sens positif.  $A, B, C, D$  sont les centres des tourbillons (Fig. 2).

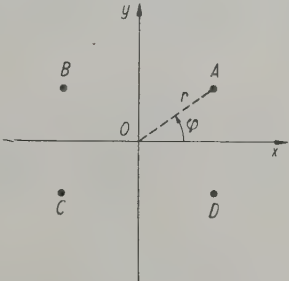


Fig. 2. Emplacement des quatre tourbillons  $A, B, C, D$  du potentiel

$$\Phi(z) = iM \log \frac{(z-A)(z-C)}{(z-B)(z-D)}.$$

Nous utiliserons ensuite la représentation conforme définie par:

$$z = \frac{1}{2} \left( Z + \frac{R^2}{Z} \right). \tag{2}$$

La portion d'axe réel obtenue quand  $z$  varie de  $-1$  à  $+1$  est transformée en une demi-circonférence de centre  $O$  et de rayon  $R$ . En effet, si

$$Z = R e^{i\Theta}, \quad \Theta \text{ variant de } \pi \text{ à } 0,$$

$$z = R \cos \Theta \quad \text{varie de } -1 \text{ à } +1.$$

Aux points  $A, B, C, D$  correspondent les points  $A_1, B_1, C_1, D_1$  dont les positions sont données expérimentalement et varient avec  $R$  et l'amplitude du mouvement vibratoire (Fig. 3).

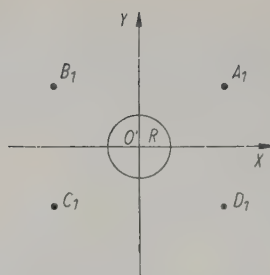


Fig. 3. Emplacement des quatre tourbillons avec un obstacle cylindrique, après transformation.

S'il est facile de construire les lignes de courant provenant du potentiel (1), la transformation (2) donne des calculs pénibles. On peut procéder autrement, bien que les résultats soient les mêmes. Associons aux tourbillons  $A, B, C, D$  leurs images  $A', B', C', D'$  par rapport au cercle  $R$  (Fig. 4). Le nouveau potentiel sera:

$$\Phi_1(z) = iM \log \frac{(z-A)(z-C)(z-B')(z-D')}{(z-B)(z-D)(z-A')(z-C')}$$

dans lequel

$$A' = \frac{R^2}{r} (\cos \varphi + i \sin \varphi)$$

et de même pour  $B', C', D'$ . Les lignes de courant seront définies par:

$$\frac{[(\varrho^2 + r^2)^2 - 4r^2\varrho^2 \cos^2(\Theta - \varphi)] \left[ \left( \varrho^2 + \frac{R^4}{r^2} \right)^2 - 4 \frac{R^4}{r^2} \varrho^2 \cos^2(\Theta + \varphi) \right]}{[(\varrho^2 + r^2)^2 - 4r^2\varrho^2 \cos^2(\Theta + \varphi)] \left[ \left( \varrho^2 + \frac{R^4}{r^2} \right)^2 - 4 \frac{R^4}{r^2} \varrho^2 \cos^2(\Theta - \varphi) \right]} = \text{Constante} = K.$$

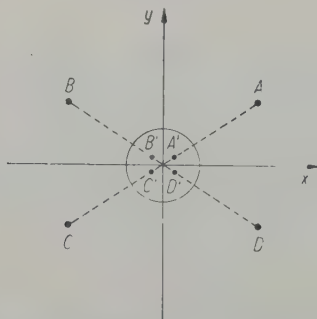


Fig. 4. Les quatre tourbillons de la Fig. 2 et leurs images par rapport à la trace du cylindre obstacle.

Pour  $K=1$ , on a comme ligne de courant, non seulement les axes, mais aussi le cercle  $\varrho=R$ ; car, alors, les deux fractions dont l'expression ci-dessus est le produit sont inverses l'une de l'autre. Nous ne garderons comme lignes de courant que celles qui sont extérieures au cercle  $R$ . On construira séparément les familles de courbes:

$$u = \frac{(\varrho^2 + r^2)^2 - 4r^2\varrho^2 \cos^2(\Theta - \varphi)}{(\varrho^2 + r^2)^2 - 4r^2\varrho^2 \cos^2(\Theta + \varphi)}$$

et

$$v = \frac{\left( \varrho^2 + \frac{R^4}{r^2} \right)^2 - 4 \frac{R^4}{r^2} \varrho^2 \cos^2(\Theta - \varphi)}{\left( \varrho^2 + \frac{R^4}{r^2} \right)^2 - 4 \frac{R^4}{r^2} \varrho^2 \cos^2(\Theta + \varphi)}.$$

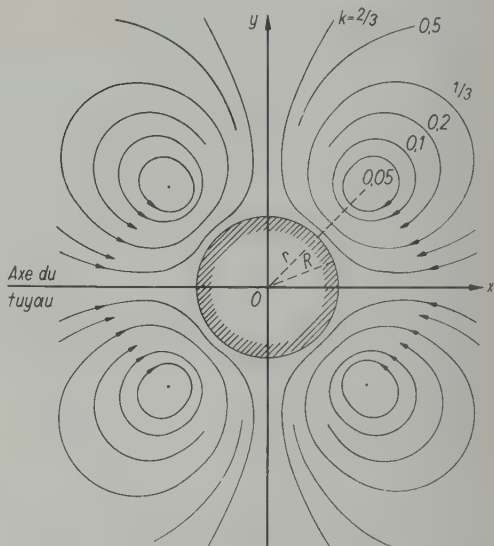


Fig. 5. Circulations pour un obstacle cylindrique.

On prendra ensuite les points d'intersection tels que  $u/v=K$ . La deuxième famille est d'ailleurs homothétique de la première dans le rapport  $R^2/r^2$ , ce qui simplifie les calculs.

Les courbes de la figure 5 ont été construites pour  $\varphi=45^\circ$  et  $R/r=1/2$ .

Lame mince (Fig. 6)

On peut négliger l'épaisseur lorsqu'elle est inférieure à 0,1 mm.

Le potentiel (1) convient;  $r$  et  $\varphi$  sont fonctions de la hauteur de la lame et de l'amplitude.

Les courbes de la figure 7 ont été construites en prenant  $\varphi = \arctg 2$ .

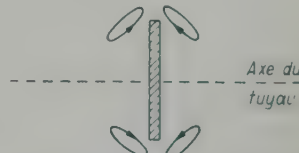


Fig. 6. Ellipses stationnaires; l'obstacle est une lame mince perpendiculaire au plan de la figure.



On pourrait aussi se servir des courbes précédentes (Fig. 5) en leur appliquant la transformation définie par :

$$Z = \frac{z^2 - R^2}{2z}$$

qui remplace le demi-cercle supérieur  $z = Re^{i\theta}$  par le segment imaginaire de 0 à 1 parcouru deux fois, car on a alors :

$$Z = R \frac{e^{i\theta} - 1}{2e^{i\theta}} = i R \sin \theta.$$

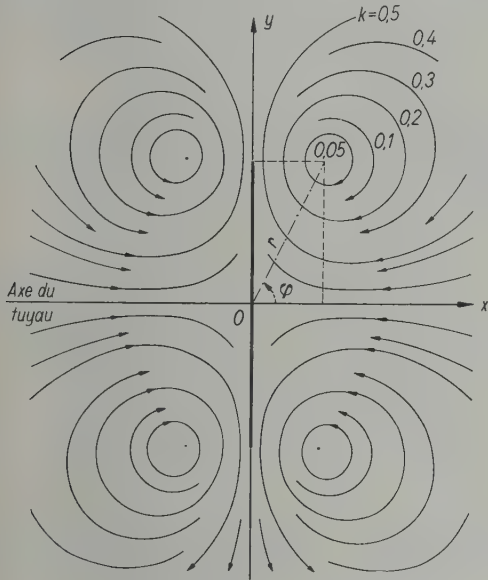


Fig. 7. Circulations pour une lame mince.

Angle solide  $2\alpha$ , disposé symétriquement par rapport à l'axe du tuyau (Fig. 8). Soit le potentiel complexe :

$$\Phi_2(z) = iM \log \frac{z-A}{z-B}$$

dans lequel

$$A = r (\cos \varphi + i \sin \varphi) = re^{i\varphi} \text{ et } B = re^{i(2\pi - \varphi)}.$$

La représentation conforme :

$$Z = z^{1-\alpha/\pi}$$

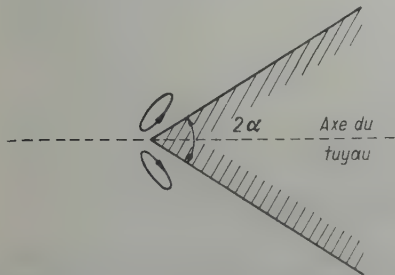


Fig. 8. Ellipses stationnaires; l'obstacle est un angle dièdre  $2\alpha$ .

fera correspondre au plan tout entier des  $z$ , un angle  $2\pi - 2\alpha$  dans le plan des  $Z$ . Les courbes de la figure 9 sont construites pour  $\alpha = \pi/4$  et  $\varphi = \pi/4$ .

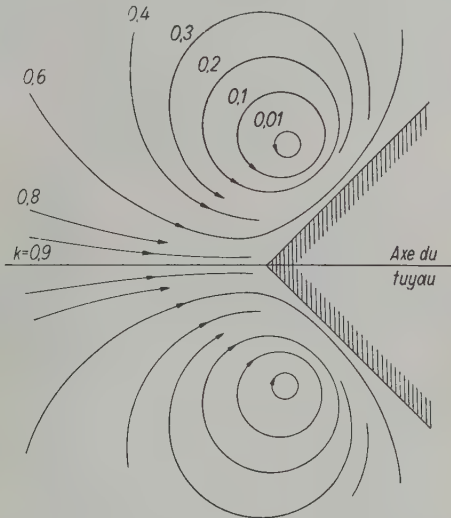


Fig. 9. Circulations pour un angle solide.

Lame plus épaisse (Fig. 10). L'épaisseur étant comprise entre 0,1 mm et 2 mm, on a quatre tourbillons. Il suffirait d'appliquer, à un potentiel à huit tourbillons convenablement disposés, une transformation remplaçant l'axe réel par un rectangle.

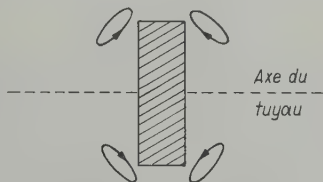


Fig. 10. Ellipses stationnaires; l'obstacle est une lame d'épaisseur moyenne.

a) Si la lame est assez haute, plus de 2 cm par exemple, on peut considérer les phénomènes de chacune de ses extrémités comme indépendants, à condition de ne pas trop s'éloigner du bout de la lame. Dans ce cas, la transformation conforme consiste à obtenir une demi-bande, ou, si l'on veut, un rectangle dont deux sommets sont rejetés à l'infini.

On utilisera la transformation définie par

$$\frac{dZ}{dz} = \sqrt{z^2 - 1}.$$

Nous prendrons comme intégrale :

$$Z = z\sqrt{z^2 - 1} - \log(z + \sqrt{z^2 - 1}) \quad (4)$$

la détermination choisie étant telle que pour  $z=0$ ,  $Z = -i\pi/2$ . On vérifie facilement que :

pour  $z$  réel, négatif et tendant vers l'infini,  $Z$  a pour partie imaginaire  $-\pi$ , sa partie réelle tendant vers plus l'infini;

pour  $z$  réel, compris entre  $-1$  et  $+1$ ,  $Z$  est imaginaire pur et varie de  $-i\pi$  à  $0$ ;

pour  $z$  réel, positif et tendant vers plus l'infini,  $Z$  est réel et tend vers plus l'infini.

On partira toujours du potentiel (1):

$$\Phi(z) = iM \log \frac{(z-A)(z-C)}{(z-B)(z-D)} \quad (1)$$

dans lequel on a pris

$$A = \sqrt{2} (1 + i)$$

et des valeurs correspondantes pour  $B$ ,  $C$  et  $D$ . On obtient ainsi les courbes de la figure 11. On

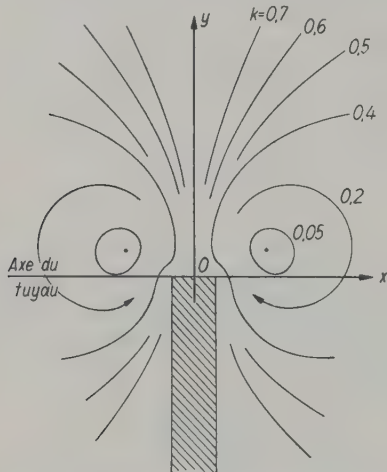


Fig. 11. Circulations pour une lame haute.

remarquera que, dès que  $|z|$  est assez grand, supérieur à 4 par exemple, on peut écrire la formule de transformation (4) en développant en série suivant les puissances de  $1/z$ , ce qui donne, en ne gardant que les premiers termes:

$$Z = z^2 - \log z - \log 2.$$

Ces courbes sont théoriques; au voisinage de l'une des arêtes de la lame, elles donnent une vitesse infinie. Dans la réalité, l'arête est toujours plus ou moins arrondie; les courbes dessinées sont des courbes limites.

b) Si les phénomènes aux extrémités ne peuvent plus être considérés comme indépendants, il faut une transformation faisant correspondre au demi-plan supérieur des  $z$  l'extérieur d'un rectangle fini.

Par analogie avec la formule de SCHWARTZ:

$$\frac{dZ}{dz} = \frac{1}{\sqrt{(z^2 - a^2)(z^2 - b^2)}}$$

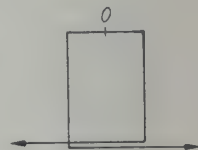
qui fait correspondre au demi-plan une infinité

de rectangles, conséquence de la double périodicité des fonctions elliptiques, considérons:

$$\frac{dZ}{dz} = \sqrt{(z^2 - a^2)(z^2 - b^2)}.$$

Fig. 12. Transformation de l'axe réel pour

$$\frac{dZ}{dz} = \sqrt{(z^2 - a^2)(z^2 - b^2)}.$$



L'axe réel des  $z$  est transformé en le contour de la figure 12, contour qui s'étend à l'infini. Prenons:

$$\frac{dZ}{dz} = f(z) \sqrt{(z^2 - a^2)(z^2 - b^2)}.$$

Il est possible de choisir  $f(z)$  de manière que le rectangle se ferme. Il faudra que la fonction  $f(z)$  ne devienne infinie pour aucune valeur finie de  $z$ . Si l'on prend:

$$\frac{dZ}{dz} = \frac{1}{z^2} \cdot e^{-k \left( \frac{z^2 + 1}{z} \right)^4} \sqrt{(z^2 - a^2) \left( z^2 - \frac{1}{a^2} \right)}.$$

$k$  et  $a$  étant deux constantes positives, la deuxième inférieure à 1, on aura, en prenant des valeurs réelles pour  $z$  (Fig. 13):

$$\overline{OA} = \int_0^a \frac{1}{z^2} \cdot e^{-k \left( \frac{z^2 + 1}{z} \right)^4} \sqrt{(z^2 - a^2) \left( z^2 - \frac{1}{a^2} \right)} dz,$$

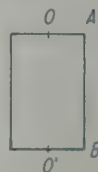
$$\overline{AB} = \int_a^{1/a} \frac{1}{z^2} \cdot e^{-k \left( \frac{z^2 + 1}{z} \right)^4} \sqrt{(a^2 - z^2) \left( z^2 - \frac{1}{a^2} \right)} dz,$$

$$\overline{BO'} = \int_{1/a}^{+\infty} \frac{1}{z^2} \cdot e^{-k \left( \frac{z^2 + 1}{z} \right)^4} \sqrt{(z^2 - a^2) \left( z^2 - \frac{1}{a^2} \right)} dz.$$

Fig. 13. Transformation de l'axe réel pour

$$\frac{dZ}{dz} = f(z) \sqrt{(z^2 - a^2)(z^2 - 1/a^2)}$$

en choisissant convenablement  $f(z)$ .



En posant dans la dernière intégrale  $z = 1/u$ , on vérifie que  $\overline{BO'} = \overline{OA}$  et donc que le rectangle se ferme.

La transformation est donc définie par:

$$Z = \int_{z_0}^z \frac{1}{z^2} \cdot e^{-k \left( \frac{z^2 + 1}{z} \right)^4} \sqrt{(z^2 - a^2) \left( z^2 - \frac{1}{a^2} \right)} dz.$$

La transformation plus simple:

$$Z = \int_{z_0}^z e^{-kz} \sqrt{(z^2 - a^2)(z^2 - b^2)} dz$$



pourrait convenir si les constantes  $a$ ,  $b$  et  $k$  étaient choisies de manière que, pour  $z$  réel, on ait :

$$\int_0^a = \int_b^{+\infty}$$

et que le rectangle ait la forme convenable.

De toutes manières, la construction des lignes de courant serait longue et pénible.

La lame plus épaisse, c'est-à-dire d'épaisseur supérieure à 2 mm (Fig. 14). Il faut rendre compte de quatre ellipses à chaque extrémité. Le problème est analogue au précédent. Il faudra seulement partir d'un potentiel ayant deux fois plus de tourbillons.

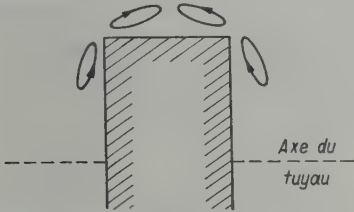


Fig. 14. Ellipses stationnaires; l'obstacle est une lame épaisse.

Les lignes de courant ainsi obtenues ne donnent pas d'ellipses, mais des courbes fermées, se rapprochant de circonférences près des centres tourbillonnaires. En réalité, les poussières sont soumises à deux mouvements: la circulation correspondant à ces tourbillons et le mouvement périodique de l'air du tuyau. Les lignes de courant proposées plus haut sont parcourues par les poussières en un temps  $\tau$  d'autant plus court qu'elles sont plus près des tourbillons. Lorsque  $\tau = T$ , période du mouvement vibratoire, on aura une ellipse stationnaire.

3. Rides de Kundt

Elles semblent bien être la conséquence de circulations analogues à celles qui produisent les ellipses stationnaires. Nous allons essayer de trouver un potentiel complexe, donnant des lignes de courant convenables.

Comme le nombre des rides est grand, nous pouvons, en dehors des extrémités, considérer ce nombre comme infini. Soit (Fig. 15) une coupe du tuyau:  $x'x$  est la trace du fond, parallèle à l'axe. Les rides, perpendiculaires à l'axe du tuyau, et donc au plan de la figure, apparaissent en  $O_1, O_2, O_3$ , etc.; leur équidistance est  $a$ . Plaçons en  $A_1, A_2, A_3$ , etc., puis en  $B_1, B_2, B_3$ , etc., des tourbillons de sens convenables, indiqués par la figure. Par rapport à l'origine  $O_1$ , les coordonnées de  $A_1$  sont  $b$  et  $c$ ; celles de  $A_2$  seront  $a+b$  et  $c$ , celles de  $A_3, 2a+b$  et  $c$ , celles de  $A_n, (n-1)a+b$

et  $c$ . Nous prendrons pour  $B_1: a-b$  et  $c$ , pour  $B_2, 2a-b$  et  $c$ , pour  $B_n, na-b$  et  $c$ . Pour que  $Ox$  soit une ligne de courant, nous ajouterons les images de ces tourbillons par rapport à cette ligne. Leurs coordonnées s'obtiennent en changeant  $c$  en  $-c$ .

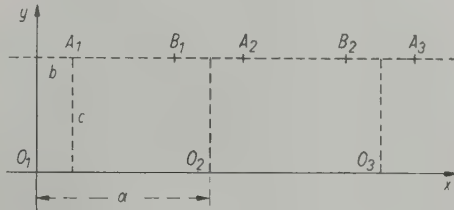


Fig. 15. Emplacement des tourbillons dans le cas des rides de KUNDT.

On aura alors le potentiel complexe:

$$f(z) = iA \sum_{n=-\infty}^{+\infty} [\log(z-b-an-ic) - \log(z+b-an-ic) - \log(z-b-an+ic) + \log(z+b-an+ic)].$$

Pour les tourbillons  $A_i$  et leurs images, nous avons remplacé  $n-1$  par  $n$ , ce qui est possible puisque  $n$  varie de moins l'infini à plus l'infini.

$$f(z) = iA \log \frac{\sin \frac{\pi}{a}(z-b-ic) \sin \frac{\pi}{a}(z+b+ic)}{\sin \frac{\pi}{a}(z+b-ic) \sin \frac{\pi}{a}(z-b+ic)}.$$

Les lignes de courant s'obtiendront en prenant la partie imaginaire de  $f(z)$ . On aura pour équation de ces lignes:

$$\frac{A}{2} \log \frac{\left[ \operatorname{ch} \frac{2\pi}{a}(y-c) - \cos \frac{2\pi}{a}(x-b) \right] \left[ \operatorname{ch} \frac{2\pi}{a}(y+c) - \cos \frac{2\pi}{a}(x+b) \right]}{\left[ \operatorname{ch} \frac{2\pi}{a}(y-c) - \cos \frac{2\pi}{a}(x+b) \right] \left[ \operatorname{ch} \frac{2\pi}{a}(y+c) - \cos \frac{2\pi}{a}(x-b) \right]} = K.$$

Pour les construire, nous poserons:

$$u = \frac{\operatorname{ch} \frac{2\pi}{a}(y-c) - \cos \frac{2\pi}{a}(x-b)}{\operatorname{ch} \frac{2\pi}{a}(y-c) - \cos \frac{2\pi}{a}(x+b)}$$

et

$$v = \frac{\operatorname{ch} \frac{2\pi}{a}(y+c) - \cos \frac{2\pi}{a}(x+b)}{\operatorname{ch} \frac{2\pi}{a}(y+c) - \cos \frac{2\pi}{a}(x-b)}.$$

Les différents points des lignes de courant s'obtiendront en considérant les points d'intersection de deux des courbes ci-dessus, telles que  $u \times v = K$ .

Prenant pour simplifier  $a=2\pi$  et  $b=c=\pi/4$ , on obtient pour les courbes  $u$ :

$$\operatorname{ch}\left(y - \frac{\pi}{4}\right) = \frac{\sqrt{2}}{2} \left( \cos x + \frac{1+u}{1-u} \sin x \right)$$

En posant  $\operatorname{tg} \varphi = \frac{1+u}{1-u}$  on a :

$$\operatorname{ch}\left(y - \frac{\pi}{4}\right) = \frac{\sqrt{2}}{2} \cdot \frac{1}{\cos \varphi} \cdot \cos(x - \varphi).$$

Pour les courbes  $v$ , on remarquera qu'on les obtient à partir des précédentes en remplaçant  $u$  par  $1/v$  et en diminuant  $y$  de  $\pi/2$ .

On obtient ainsi les courbes de la figure 16.

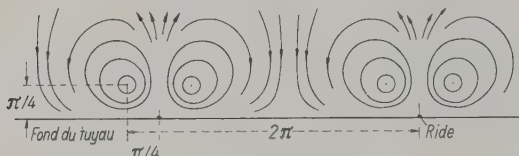


Fig. 16. Circulations des rides de KUNDT.

#### 4. Tuyau sonore avec dérivation

Les résultats expérimentaux étant les mêmes pour des formes de dérivation différentes, j'ai fait choix d'un embranchement en Y, suivant la figure 17, les deux branches faisant entre elles un angle de  $90^\circ$ . Les longueurs  $Ox = X$ ,  $Oy = Y$ ,  $Oz = Z$  sont variables au moyen de coulisses fermées à leur extrémité. J'ai utilisé les deux fréquences 100 et 300 c/s. Les résultats sont tout à fait comparables. Les courbes tracées ici correspondent à  $N = 300$  c/s.

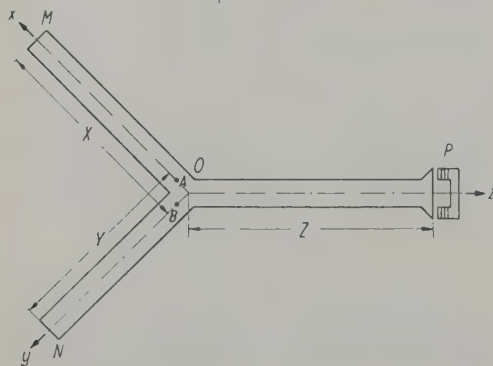


Fig. 17. Tuyau avec dérivation en Y.

a) *Amplitudes.* Elles sont mesurées en  $A$  et  $B$ , à 3 cm du centre de branchement. Le système est symétrique par rapport à  $Ox$  et  $Oy$ . Les courbes donnent le relief de l'amplitude  $A$ , dans la branche  $Ox$ , suivant les valeurs de  $Ox = X$  et  $Oy = Y$ ,  $Oz = Z$  ayant une valeur déterminée. La valeur réelle des amplitudes n'est pas indiquée, les valeurs proportionnelles suffisent.

Si  $Oz = Z = \lambda/4$  ou  $(2k+1)\lambda/4$ ,  $\lambda$  étant la longueur d'onde, on obtient les courbes de la figure 18.

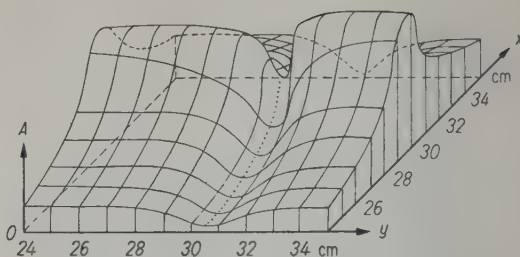


Fig. 18. Courbes expérimentales pour  $Z = \lambda/4$ .

Les amplitudes sont d'autant plus grandes que la branche  $Ox$  a une longueur plus proche de  $\lambda/4$ , et, pour une valeur donnée de cette longueur, d'autant plus petites que l'autre branche,  $Oy$  est plus voisine de  $\lambda/4$ . Tout se passe comme si l'onde stationnaire située dans  $Oz$  se partageait en deux parties, l'une dans  $Ox$ , l'autre dans  $Oy$ .

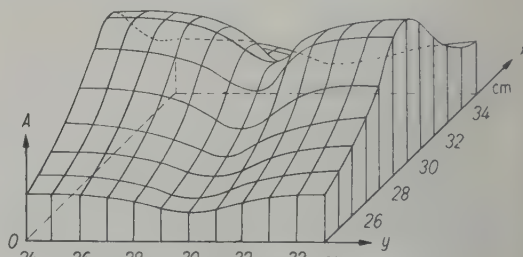


Fig. 19. Courbes théoriques pour  $Z = \lambda/4$ .

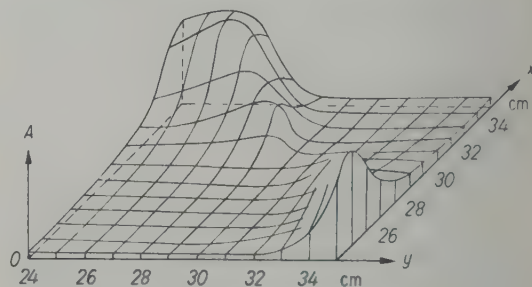


Fig. 20. Courbes expérimentales pour  $Z = \lambda/2$ .

Si  $Oz = Z = \lambda/2$  ou  $k\lambda/2$ , on obtient les courbes de la figure 20. La série de maximums obtenus pour  $X + Y = \text{constante} = \lambda/2$ , montre que l'ensemble tend à vibrer entre  $Ox$  et  $Oy$ ,  $Oz$  étant alors désaccordé.

Pour des positions intermédiaires, les deux aspects se présentent, avec prédominance du second dès que l'on s'écarte de quelques centimètres de  $Z = \lambda/4$ . Les courbes de la figure 22 correspondent à  $Z = \lambda/4 + \lambda/60$ .

Il est possible de parler d'effet « filtre ». L'amplitude dans la branche  $Ox$  est minimum lorsque  $Oy = Y = \lambda/4$ . Dans le cas où ce minimum est le



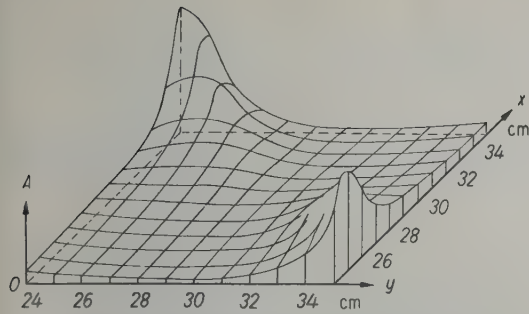


Fig. 21. Courbes théoriques pour  $Z = \lambda/2$ .

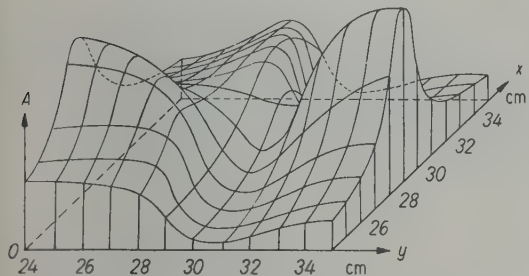


Fig. 22. Courbes expérimentales pour  $Z = \lambda/4 + \lambda/60$ .

moins marqué, le rapport des amplitudes est  $1/2$ , soit pour l'énergie un rapport  $1/4$ . Ce rapport est presque toujours beaucoup plus petit.

*b) Phases.* Les capsules manométriques à miroir étant branchées aux extrémités  $M$  et  $N$ , les différences de phases entre les deux branches  $Ox$  et  $Oy$  ne dépendent pas de la longueur  $Z$  (Fig. 24). Il n'en est évidemment pas de même des différences de phases entre  $M$  ou  $N$  et le téléphone  $P$ . Les mesures peuvent être contrôlées en vérifiant la relation :

$$\varphi_{M, N} = \varphi_{M, P} + \varphi_{P, N}.$$

Nous avons remarqué que pour  $X + Y = \lambda/2$ , les deux branches de l' $Y$  semblaient vibrer ensemble, indépendamment de  $Oz$ , surtout quand la longueur de cette dernière branche était voisine de  $\lambda/2$ . La différence de phase entre  $M$  et  $N$  devrait alors être égale à  $\pi$ ; ce qui ne correspond pas du tout à l'expérience.

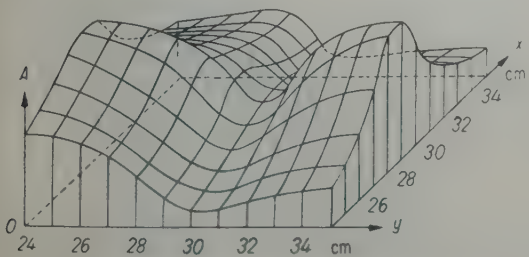


Fig. 23. Courbes théoriques pour  $Z = \lambda/4 + \lambda/60$ .

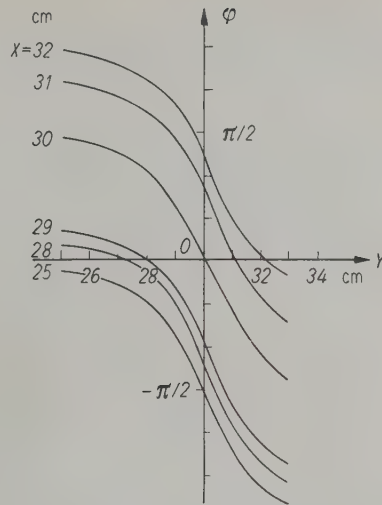


Fig. 24. Courbes expérimentales des différences de phases.

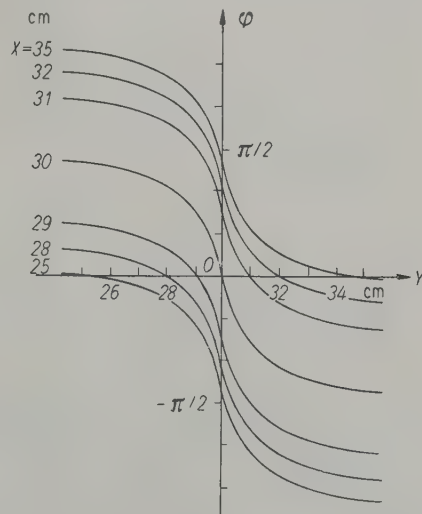


Fig. 25. Courbes théoriques des différences de phases.

### Tuyau unique. Calcul des amplitudes

Comme préliminaire au calcul des amplitudes et phases pour un tuyau avec branchement, voyons ce qui se passe pour un tuyau unique dont on fait varier la longueur  $L$  (Fig. 26).

Les amplitudes ont été mesurées, pour la fréquence 100 c/s, en différents points: depuis le fond, opposé au téléphone, jusqu'à 80 cm de ce point, ce qui représente environ un quart de longueur d'onde. Pour une longueur donnée du tuyau, on obtient une variation sinusoidale. Soit



Fig. 26. Tuyau unique.

$x$  la distance du fond du tuyau au point d'observation, l'amplitude est de la forme:

$$u_0 = k \sin 2\pi \frac{x}{\lambda}$$

Le coefficient  $k$  dépend de la longueur  $L$  du tuyau. Pour différentes valeurs de  $L$  on obtient les courbes de la figure 27.

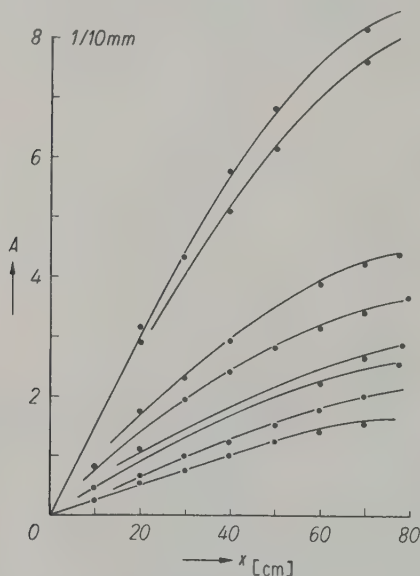


Fig. 27. Amplitudes du mouvement vibratoire en fonction de la distance du point d'observation au fond du tuyau, pour différentes valeurs de  $L$  la longueur totale de ce tuyau. Courbes expérimentales.

Si nous considérons les amplitudes en un point donné du tuyau ( $x=20$  cm par exemple), on obtient les points placés sur la figure 28 et correspondant à différentes valeurs de  $L$ . On voit que la résonance du tuyau a lieu pour une longueur voisine de 160 cm, légèrement inférieure à une demi-longueur d'onde.

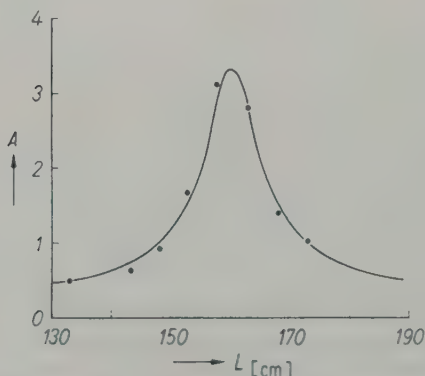


Fig. 28. Amplitudes à 20 cm du fond en fonction de la longueur du tuyau.

Soit  $u_1$  l'onde progressive émise par la plaque du téléphone:

$$u_1 = \sin 2\pi \left( \frac{t}{T} - \frac{L}{\lambda} + \frac{x}{\lambda} \right)$$

en prenant, pour simplifier, l'amplitude égale à 1. Cette onde se réfléchit sur le fond et donne:

$$u_2 = -\sin 2\pi \left( \frac{t}{T} - \frac{L}{\lambda} - \frac{x}{\lambda} \right)$$

d'où l'onde résultante:

$$u = u_1 + u_2 = 2 \cos 2\pi \left( \frac{t}{T} - \frac{L}{\lambda} \right) \sin 2\pi \frac{x}{\lambda}.$$

A une distance donnée du fond du tuyau, l'amplitude  $\sin 2\pi x/\lambda$  ne dépend pas de  $L$ . Faisons intervenir les autres réflexions. Admettons que la réflexion sur la plaque téléphonique se fasse comme sur une paroi rigide, on aura:

$$u_3 = \sin 2\pi \left( \frac{t}{T} - \frac{3L}{\lambda} + \frac{x}{\lambda} \right)$$

puis,

$$u_4 = -\sin 2\pi \left( \frac{t}{T} - \frac{3L}{\lambda} - \frac{x}{\lambda} \right)$$

et ainsi de suite. Groupant les termes deux à deux et additionnant, on aura:

$$\begin{aligned} u &= 2 \cos 2\pi \left( \frac{t}{T} - \frac{L}{\lambda} \right) \sin 2\pi \frac{x}{\lambda} + \\ &+ 2 \cos 2\pi \left( \frac{t}{T} - \frac{3L}{\lambda} \right) \sin 2\pi \frac{x}{\lambda} + \dots \\ u &= 2 \sin 2\pi \frac{x}{\lambda} \left[ \cos 2\pi \left( \frac{t}{T} - \frac{L}{\lambda} \right) + \right. \\ &\left. + \cos 2\pi \left( \frac{t}{T} - \frac{3L}{\lambda} \right) + \dots \right]. \end{aligned}$$

L'expression entre crochets est la partie réelle de

$$\exp \left[ i 2\pi \left( \frac{t}{T} - \frac{L}{\lambda} \right) \right] + \exp \left[ i 2\pi \left( \frac{t}{T} - \frac{3L}{\lambda} \right) \right] + \dots$$

C'est une progression géométrique de raison égale  $\exp [i 2\pi (-2L/\lambda)]$ . Mais, comme le module de chaque terme est égal à 1, la série est divergente et l'amplitude infinie.

En réalité, l'onde s'amortit. Au lieu de supposer cet amortissement proportionnel au parcours, admettons, ce qui revient en gros au même, que, chaque deux réflexions, l'amplitude soit multipliée par  $\alpha$ ,  $\alpha$  étant positif et inférieur à 1. On aura alors pour somme des termes de la progression:

$$S = \frac{\exp \left[ i 2\pi \left( \frac{t}{T} - \frac{L}{\lambda} \right) \right]}{1 - \alpha \cdot \exp (-i 2\pi 2L/\lambda)}$$

d'où l'on tire:



$$u = 2 \sin 2\pi \frac{x}{\lambda} \cdot \frac{\cos 2\pi \left( \frac{t}{T} - \frac{L}{\lambda} \right) \cdot \left( 1 - \alpha \cos 2\pi \frac{2L}{\lambda} \right) + \alpha \sin 2\pi \frac{2L}{\lambda} \sin 2\pi \left( \frac{t}{T} - \frac{L}{\lambda} \right)}{1 + \alpha^2 - 2\alpha \cos 2\pi \frac{2L}{\lambda}}.$$

Si on pose :

$$u = A \sin \left[ 2\pi \left( \frac{t}{T} - \frac{L}{\lambda} \right) - \varphi \right]$$

on a l'amplitude  $A$  donnée par :

$$A^2 = \frac{4 \sin^2 2\pi x/\lambda}{1 + \alpha^2 - 2\alpha \cos 2\pi 2L/\lambda} = k^2 \sin^2 2\pi x/\lambda$$

avec

$$k = \frac{2}{\sqrt{1 + \alpha^2 - 2\alpha \cos 2\pi 2L/\lambda}}.$$

La courbe de la figure 28 est tracée pour  $\alpha = 0,8$ ; elle rend compte de façon satisfaisante des résultats expérimentaux.

Calcul des amplitudes et des phases dans un tuyau en Y

a) *Amplitudes.* Pour rendre compte des courbes obtenues en faisant varier  $X$ ,  $Y$  et  $Z$ , faisons les hypothèses suivantes :

Soit :

$$u_0 = \sin 2\pi \left( \frac{t}{T} - \frac{z}{\lambda} \right)$$

l'onde progressive émise par la plaque du téléphone,  $z$  étant compté à partir de la plaque, vers O (Fig. 17). L'amplitude est prise égale à 1. En O, elle se partage en deux ondes :

$$u_{0x} = k \sin 2\pi \left( \frac{t}{T} - \frac{Z}{\lambda} - \frac{x}{\lambda} \right)$$

et

$$u_{0y} = k \sin 2\pi \left( \frac{t}{T} - \frac{Z}{\lambda} - \frac{y}{\lambda} \right).$$

$k$  étant un nombre positif inférieur à 1. Ces deux ondes vont se réfléchir, respectivement en M et N, revenir en O, s'y partager de nouveau et ainsi de suite. Admettons qu'à chaque réflexion l'amplitude soit multipliée par  $\alpha$ , nombre positif, inférieur à 1, pour tenir compte de l'amortissement. On aura le schéma suivant, pour la branche  $Ox$  :

Onde une fois partagée, allant de O vers M :

$$k \sin 2\pi \left( \frac{t}{T} - \frac{Z}{\lambda} - \frac{x}{\lambda} \right).$$

Onde une fois partagée, réfléchie en M :

$$-\alpha k \sin 2\pi \left( \frac{t}{T} - \frac{Z}{\lambda} - \frac{2X}{\lambda} + \frac{x}{\lambda} \right).$$

Onde deux fois partagée, de O vers M :

$$\alpha k^2 \sin 2\pi \left( \frac{t}{T} - \frac{Z}{\lambda} - \frac{2Y}{\lambda} - \frac{x}{\lambda} \right).$$

Onde deux fois partagée, réfléchie :

$$-\alpha^2 k^2 \sin 2\pi \left( \frac{t}{T} - \frac{Z}{\lambda} - \frac{2Y}{\lambda} - \frac{2X}{\lambda} + \frac{x}{\lambda} \right).$$

Exprimons les ondes sous forme complexe. Faisons  $x=0$ , ce qui correspond à peu près au point d'observation, près de O. Posons :

$$2\pi \left( \frac{t}{T} - \frac{Z}{\lambda} \right) = a, \quad 2\pi \frac{2X}{\lambda} = u,$$

$$2\pi \frac{2Y}{\lambda} = v, \quad 2\pi \frac{2Z}{\lambda} = w.$$

On aura pour somme de ces différentes ondes, allant de O vers M :

$$S_0 = k e^{ia},$$

$$S_1 = \alpha k^2 e^{i(a-v)},$$

$$S_2 = \alpha^3 k^3 [e^{i(a-u-v)} + e^{i(a-v-w)} + e^{i(a-u-w)}],$$

ou

$$S_2 = \alpha^2 k^3 e^{ia} [e^{-i(u+v)} + e^{-i(v+w)} + e^{-i(u+w)}].$$

et ainsi de suite. Les ondes réfléchies s'obtiennent en multipliant les précédentes par  $-\alpha e^{-iu}$ .

On vérifie la relation de récurrence :

$$S_n - \alpha^2 k^2 [e^{-i(u+v)} + e^{-i(v+w)} + e^{-i(u+w)}] S_{n-2} + 2\alpha^3 k^3 e^{-i(u+v+w)} S_{n-3}$$

ou :

$$S_n = A S_{n-2} + B S_{n-3}$$

en posant :

$$A = \alpha^2 k^2 [e^{-i(u+v)} + e^{-i(v+w)} + e^{-i(u+w)}]$$

et

$$B = 2\alpha^3 k^3 e^{-i(u+v+w)}.$$

En groupant les  $S_n$  deux par deux (pairs et impairs), on obtient leur somme sous forme de séries géométriques, convergentes grâce aux facteurs  $k$  et  $\alpha$ , inférieurs à 1. On trouve ainsi :

$$S = \frac{S_2 + S_1 + (1-A) S_0}{1-A-B}.$$

En y ajoutant les ondes réfléchies, on obtient finalement :

$$S = \frac{e^{ia} k (1 - \alpha e^{-iu}) (1 + \alpha k e^{-iv})}{1 - \alpha^2 k^2 [e^{-i(u+v)} + e^{-i(v+w)} + e^{-i(u+w)}] - 2\alpha^3 k^3 e^{-i(u+v+w)}}.$$

La partie imaginaire de cette expression représente les phénomènes. Elle est de la forme:

$$u = A \sin \left[ 2\pi \left( \frac{t}{T} - \frac{Z}{\lambda} \right) + \psi \right].$$

L'amplitude  $A$  est le module de  $S$ ;  $\psi$  est l'argument, changé de signe du coefficient de  $e^{ia}$ .

Soit  $Z = \lambda/4$ ; on aura:

$$S = - \frac{e^{ia} k (1 - \alpha e^{-iu}) (1 + \alpha k e^{-iv})}{1 - \alpha^2 k^2 [e^{-i(u+v)} - e^{-iv} - e^{-iu}] + 2\alpha^3 k^3 e^{-i(u+v)}}.$$

Les courbes de la figure 19 sont construites pour  $\alpha k = 0,9$  et  $\alpha = 0,99$ .

Soit  $Z = \lambda/2$ ; on aura:

$$S = \frac{e^{ia} k (1 - \alpha e^{-iu}) (1 + \alpha k e^{-iv})}{1 - \alpha^2 k^2 (e^{-iv} + e^{-iu}) - \alpha^2 k^2 (1 + 2\alpha k) e^{-i(u+v)}}.$$

D'où les courbes de la figure 21.

Enfin, pour  $Z = \lambda/4 + \lambda/60$ , on a les courbes de la figure 23.

Les courbes théoriques et expérimentales sont comparables; les premières rendent compte de l'allure des phénomènes sinon de leur grandeur exacte.

b) Phases. A l'extrémité M de  $Ox$ , on a

$$S' = S_1 e^{-iu/2}$$

pour les ondes allant de  $O$  vers  $x$ . De même, pour les ondes réfléchies:

$$S'' = S_2 e^{iu/2}.$$

D'où, pour l'ensemble:

$$S_x = \frac{e^{ia} k e^{-iu/2} (1 - \alpha) (1 + \alpha k e^{-iv})}{1 - \alpha^2 k^2 [e^{-i(u+v)} + e^{-i(v+w)} + e^{-i(u+w)}] - 2\alpha^3 k^3 e^{-i(u+v+w)}}$$

et une formule analogue pour  $S_y$ .

La différence de phase entre les mouvements des extrémités des deux branches sera égale à la différence des arguments des deux expressions  $S_x$  et  $S_y$ . Elle sera indépendante de  $w$ , donc de  $Z$ .

La phase de  $Oy$ , diminuée de la phase de  $Ox$ , donne:

$$\varphi = \arctg \frac{(1 - \alpha^2 k^2) (\operatorname{tg} u/2 - \operatorname{tg} v/2)}{(1 + \alpha k)^2 + (1 - \alpha k)^2 \operatorname{tg} u/2 \cdot \operatorname{tg} v/2}$$

ou encore:

$$\varphi = \arctg \frac{1 - \alpha k}{1 + \alpha k} \cdot \operatorname{tg} \frac{u}{2} - \arctg \frac{1 - \alpha k}{1 + \alpha k} \cdot \operatorname{tg} \frac{v}{2}.$$

Les courbes  $u = \text{constante}$  sont égales et translatées suivant l'axe des phases. (Courbes de la figure 25.)

Si les courbes théoriques ont la même allure que les courbes expérimentales, elles en sont plus éloignées cependant que les courbes des amplitudes; on ne peut les utiliser pour représenter les phénomènes en détail.

Les mesures sont d'ailleurs moins précises que dans le cas des amplitudes. L'expression:

$$\sin \varphi = \frac{ab}{AB}$$

où  $a$  et  $b$  sont les axes de l'ellipse de Lissajous vue à travers les deux miroirs,  $A$  et  $B$  les amplitudes mesurées suivant les axes des miroirs, montre que l'erreur  $d\varphi$  sur la phase peut devenir infinie; cela a lieu lorsque  $\varphi = \pi/2$ . On a en effet:

$$d\varphi = \left( \frac{|da|}{a} + \frac{|db|}{b} + \frac{|dA|}{A} + \frac{|dB|}{B} \right) \operatorname{tg} \varphi.$$

Lorsqu'on veut étudier avec quelques détails les mouvements vibratoires d'une certaine cavité, on se trouve toujours loin des conditions idéales de la théorie élémentaire. Des hypothèses plus ou moins ingénieuses permettent de rendre compte assez bien des phénomènes observés; mais on n'atteint jamais des résultats pleinement satisfaisants.

(Reçu le 8 avril, 1952).



# MEASUREMENTS OF SOUND ABSORPTION IN WATER AND IN AQUEOUS SOLUTIONS OF ELECTROLYTES

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## Summary

By means of four types of apparatus, working in successive frequency ranges, absorption measurements were made in the large frequency range  $4 \cdot 10^3$  to  $10^8$  c/s. For the lowest frequencies (4–50 kc/s) the absorption was determined from the decay of single normal modes of oscillation of a spherical vessel, filled with the solution. In the medium range (50–1000 kc/s) a reverberation method was applied. Above 1 Mc/s the attenuation of progressive waves was measured with the optical method, using two different techniques (3–15 Mc/s and 20–100 Mc/s).

The measurements in water yield a value  $\alpha/\nu^2 = 25 \cdot 10^{-15}$  s<sup>2</sup>/m at 20°C, independent of frequency down to 100 kc/s.

The experimental results with electrolytes permit a number of fundamental conclusions with respect to the dependence of the absorption on frequency, on concentration, temperature and pH-value of the solutions and on the properties of the ions such as valency and ion radius.

The results indicate relaxation processes. As an attempt of interpretation, four models are discussed: 1., excitation of molecular degrees of freedom, 2., hydration of the ions, 3., formation of ion associates, and 4., hydrolysis, the latter being the most probable one.

## Sommaire

On a fait, au moyen de quatre appareils de mesure travaillant dans des gammes de fréquences se succédant, des mesures d'absorption dans le large domaine de fréquences de  $4 \cdot 10^3$  à  $10^8$  Hz. Dans le cas des fréquences les plus basses (4 à 50 kHz), on a déterminé l'absorption par mesure de la durée d'affaiblissement des oscillations propres individuelles d'un récipient sphérique rempli du liquide à étudier. Dans le cas des fréquences moyennes (50 à 1000 kHz), on a employé une méthode de réverbération. Au-delà de 1 MHz, on a mesuré l'amortissement d'ondes progressives par la méthode optique, au moyen de deux dispositifs différents (de 3 à 15 MHz et de 20 à 100 MHz).

Les mesures faites sur l'eau pure ont montré à nouveau l'indépendance, vis-à-vis de la fréquence, de la valeur bien connue  $\alpha/\nu^2 = 25 \cdot 10^{-15}$  s<sup>2</sup>/m (à 20°C), jusqu'à 100 kHz.

Les résultats obtenus avec des solutions électrolytiques conduisent à un certain nombre de conclusions fondamentales en ce qui concerne la variation de l'absorption avec la fréquence, la concentration, la température et le pH de la solution, ainsi qu'avec les propriétés ioniques comme la valence et le rayon des ions.

Les résultats mettent en évidence des processus de relaxation. On a cherché à les interpréter au moyen de quatre modèles: 1. excitation des degrés de liberté moléculaires, 2. hydratation des ions, 3. formation d'associations d'ions, et 4. hydrolyse. Le dernier modèle paraît le plus probable.

## Zusammenfassung

Mit Hilfe von vier Meßapparaturen, die in aufeinanderfolgenden Frequenzbereichen arbeiten, wurden Absorptionsmessungen in dem großen Frequenzbereich  $4 \cdot 10^3 \dots 10^8$  Hz gemacht. Bei den tiefsten Frequenzen (4–50 kHz) wurde die Absorption aus der Abklingzeit von einzelnen Eigenschwingungen eines mit der zu messenden Flüssigkeit gefüllten kugelförmigen Gefäßes bestimmt. Im mittleren Frequenzbereich (50–1000 kHz) wurde eine Nachhallmethode angewendet. Oberhalb 1 MHz wurde die Dämpfung mit der optischen Methode an fortschreitenden Wellen gemessen, wobei zwei verschiedene Apparaturen benutzt wurden (3–15 MHz und 20–100 MHz).

Die Messungen an reinem Wasser ergeben die Frequenzunabhängigkeit des bekannten Wertes  $\alpha/\nu^2 = 25 \cdot 10^{-15}$  s<sup>2</sup>/m (20°C) bis hinab zu 100 kHz.

Die Meßergebnisse an Elektrolytlösungen erlauben eine Anzahl von grundlegenden Schlüssen in Bezug auf die Abhängigkeit der Absorption von der Frequenz, von Konzentration, Temperatur und pH-Wert der Lösung sowie von Ioneigenschaften wie Wertigkeit und Ionenradius.

Die Ergebnisse deuten auf Relaxationsprozesse. Als Deutungsversuche werden vier Modelle diskutiert: 1. Anregung von molekularen Freiheitsgraden, 2. Ionenhydratation, 3. Bildung von Ionenassoziaten, und 4. Hydrolyse, wobei das letzte das wahrscheinlichste ist.

## 1. Introduction

According to the "classical" theory of STOKES, sound waves in liquids suffer because of shear

forces in the liquid an energy loss which causes an absorption coefficient<sup>1</sup>  $\propto$  proportional to the

<sup>1</sup> For the definition of  $\alpha$  see 3, a.

square of frequency  $\nu$ . The characteristic constant  $\alpha/\nu^2$  is given by the shear viscosity of the liquid. Only for a few liquids such as Hg the losses due to heat conduction play an important part, which, having the same frequency dependence, may be taken into account by an increase of the classical value.

In nearly all liquids the sound absorption considerably exceeds the classical value, thus indicating that there exist other energy losses in the liquids due to dynamic compression which may formally be ascribed to a volume or pressure viscosity. Such sound energy losses may be caused by the retarded (irreversible) transition of energy between different degrees of freedom, or chemical or structural arrangements of the molecules, i.e. by molecular relaxation processes as the excitation of rotational or vibrational degrees of freedom of molecules (eg. in CS<sub>2</sub> [2]), chemical reactions (e.g. hydrolysis [3]), the change of molecules to interlattice positions in the quasi-crystalline structure of liquids [4], [5], the aggregation of molecules to double-molecules as in acetic acid [6] or to 8-molecule aggregates as in H<sub>2</sub>O [7], the reaction between ions (dissociation) [8], the hydration [7], [9], etc.

When in a sound wave the thermodynamic equilibrium between two states of the molecules of a liquid (which determines the density) is disturbed by compression or alteration of temperature, it re-establishes itself with a finite time constant  $\tau$ , and a phase difference between pressure and density results, which means an additional damping (relaxation absorption) of the sound wave, given by  $\alpha_{rel.} = A\omega^2/(1 + \omega^2\tau^2)$ , where  $\omega = 2\pi\nu$ . Characteristic for a relaxation process is the relaxation frequency  $\nu_m = 1/2\pi\tau$  far below which ( $\omega \ll 1/\tau$ ) the energy loss increases with  $\nu$  and  $\alpha_{rel.}$  is proportional to the square of frequency, whilst at frequencies far above  $\nu_m$  ( $\omega \gg 1/\tau$ ) the energy transition becomes very incomplete, so that  $\alpha$  becomes constant. The total absorption of a liquid may be composed of a sum of relaxation processes

$$\alpha = \sum_{i=1}^n A_i \frac{\omega^2}{1 + \omega^2\tau_i^2} + B\omega^2$$

where the second term involves the classical losses. With decreasing frequency the value  $\alpha/\nu^2$  has a flat steplike increase for every relaxation frequency passed. From the value of the relaxation frequency and from its alteration with temperature, conclusions may be drawn on the nature of the energy transition as has been discussed by KNESER [1]. The measurement of sound absorption therefore has often been used for

studying the properties of liquids. In the present work this method is applied to water and aqueous solutions of electrolytes.

## 2. Measurements by other authors

### a) Absorption measurements in pure water

An important part of the present experiments is concerned with measurements of sound absorption in pure water, because of the interest in the properties of water, but also because it serves as a solvent for the electrolytes and as a standard for the measurement of sound absorption.

In the frequency range from 5 to 300 Mc/s a large number of fairly exact measurements of sound absorption in pure water has been made [11]–[21]. The results (collected by SETTE [10]) give an absorption proportional to the square of frequency corresponding to a value  $\alpha/\nu^2 = 25 \cdot 10^{-15} \text{ s}^2/\text{m}$  at 20°C, a value 3 times higher than the classical value. KNESER [1], HALL [4] and GIERER and WIRTZ [5] ascribed this excess absorption to a structure relaxation. At lower frequencies, however, due to greater demands on measuring technique, it is only in the last few years that reliable results have been published. When the present work was started, the only reliable values known here at frequencies below 1 Mc/s were determined at 14°C by SKUDRZYK and MEYER [22], [23] using a two chamber reverberation method. If these values are reduced to 20°C with the aid of the temperature dependence, which has been determined since then at high frequencies by FOX and ROCK [16], PINKERTON [20] and SMITH and BEYER [21] and calculated by HALL [4] there is only a small deviation from the standard value, which caused KNESER [1] to suggest a relaxation frequency between 0.1 and 1 Mc/s. Measurements at 1.4 and 2 Mc/s by CLAEYS, ERRERA and SACK [24] appeared to confirm this assumption. But new measurements by MULDER [25] using the two chamber reverberation method from 0.75 to 1.5 Mc/s, by LEONARD [26] using a resonance method from 15 to 480 kc/s, by MOEN [27] using a special reverberation method above 160 kc/s, in agreement with the present measurements, using the two chamber reverberation method, fit the assumption  $\alpha/\nu^2 = 25 \cdot 10^{-15} \text{ s}^2/\text{m}$ , i.e. independent of frequency, also for frequencies down to 100 kc/s. This assumption is supported by measurements of LIEBERMANN [28] between 240 and 940 kc/s, using progressive spherical waves. Measurements of one of the authors [29] in a lake at still lower frequencies 10, 20, 40 kc/s gave only a limiting value  $\alpha/\nu^2 < 70 \cdot 10^{-15} \text{ s}^2/\text{m}$ .



b) Absorption measurements in aqueous solutions of electrolytes

It is known from many measurements (summary by SETTE [10]) that aqueous solutions of many salts have a noticeably higher absorption than pure water. Very often experiments have been made with solutions of the salts contained in sea water and similar salts at frequencies above 1 Mc/s. In particular  $\text{MgSO}_4$  solutions often have been investigated because of their strikingly large absorption: by BAZULIN [30] using the light diffraction method, by TEETER [31] using an electrical method, by BUSS [32], by CLAEYS, ERRERA, SACK [24] using the radiation pressure method, and by SMITH, BARRET, BEYER [33] using the last two methods. The value  $\alpha/\nu^2$  of these solutions was not found, as for water, practically independent of frequency, but rapidly increasing with decreasing frequency at frequencies below 1 Mc/s (SETTE [10]). This led to the suggestion that chemical relaxation processes, as theoretically treated by EINSTEIN [34] have their relaxation maximum at frequencies below 1 Mc/s. In this connection in recent years investigations have been carried out at lower frequencies, where similar difficulties arise as in the case of pure water. From measurements of the absorption of sea water by LIEBERMANN [28] with progressive waves in the sea and by LEONARD [35], [36] with a resonance method, a relaxation curve with a relaxation frequency at 130 kc/s was obtained (LIEBERMANN [8]). LIEBERMANN [8] and LEONARD, COMBS and SKIDMORE [35] recognised from LEONARD's measurements [36], in agreement with the statements of the authors [37], that this excess absorption is not due to the NaCl but to the percentage of  $\text{MgSO}_4$  present, the effect of which, however, is detrimentally influenced by the NaCl contents. LIEBERMANN [8] assumes the dissociation to be the cause of the relaxation in  $\text{MgSO}_4$  solutions and suggests proportionality of the absorption with the square root of the concentration. LEONARD and WILSON [36], [3] and the authors [37]–[41] have independently, in good agreement with each other, shown by measurements that  $\alpha/\nu^2$  depends nearly linear on concentration, and have tried to explain this fact by assuming a relaxing transition between two energy states of the ion pairs. The experimental activation energy was determined from the temperature dependence by WILSON [3] as 7.9 kcal/mole and by one of the authors [39] as 6.15 kcal/mole.

The measurements presented here had the purpose to give a sufficiently large amount of experimental data of the electrolyte absorption in dependence on valency of the electrolyte, con-

centration, pH-value, and temperature in a very large frequency range by using several methods, because each of them is applicable only in a limited frequency range.

### 3. Methods and apparatus for measuring the absorption

#### a) Choice of the method

Because the absorption and the conditions of propagation strongly depend on frequency, different methods must be used within a range of some octaves each. At frequencies above 1 Mc/s the absorption is high and can be determined from the decrease of the energy density  $E'$  in a progressive plane wave

$$E'_x = E'_0 \cdot e^{-2\alpha x}.$$

At lower frequencies this "progressive wave method" would require large transmitters and very large volumes of liquid, because of the directivity of the transmitter necessary and because the absorption generally decreases with decreasing frequency (at 100 kc/s the amplitude of a plane wave in pure water is only reduced by 10% over 1 km), and consequently can only be applied in lakes or in the sea but scarcely in laboratories. Below 1 Mc/s, therefore, it is more convenient to determine the absorption from the decay with time of the energy  $E$  of a standing wave between the boundaries of the liquids

$$E_t = E_0 \cdot e^{-2\delta t}, \text{ where } \delta = \alpha c.$$

The main difficulty of such "standing wave methods" is the elimination of the boundary losses which considerably influence the decay constant. The decay constant can be obtained either from the decay time of a single mode of oscillation of the system (liquid + vessel) or as a mean value from the reverberation time of the system when simultaneously excited to many statistically distributed normal modes of oscillation. Both methods were applied, in the frequency range 50–1000 kc/s,—where the vessels can be made large compared with the wavelength—a two chamber reverberation method and in the range 4–50 kc/s the resonance method, using a spherical resonator.

#### b) Resonance method<sup>2</sup> (spherical resonator method)

##### $\alpha$ ) Principle of the method

A resonator filled with the liquid to be investigated (aqueous solutions of electrolytes) is excited

<sup>2</sup> The equipment was built and theoretically considered by H. J. NAAKE [41]. A quite similar method was developed by LEONARD [36] and WILSON [3].

as far as possible to one single normal mode of oscillation. After stopping the excitation its decay constant  $\delta_s$ , which is determined by the liquid and by the boundary losses, is measured. The influence of the wall (boundary losses) can be eliminated by subtracting the decay constant  $\delta_w$  of the same normal mode of oscillation measured when the resonator is filled with a standard liquid of known absorption (pure water) and nearly equal velocity of sound propagation. The difference  $\alpha_{el.}$  of the absorption coefficients of the two liquids is given by

$$\alpha_{el.} = \alpha_s - \alpha_w = (\delta_s - \delta_w)/c.$$

An absolute measurement of absorption coefficients without a standard is scarcely possible with this method. As resonator a spherical glass vessel was chosen, having some advantages over other shapes of vessels: 1., because of the stability of this form the walls can be made extremely thin and deformation losses and wall friction losses become small; 2., for certain vibration patterns (purely radial vibrations) the wall friction losses are excluded; 3., an estimation of the boundary losses can be made by discussing the deviations of the sound field from that in an ideal spherical resonator.

### $\beta$ ) Experimental equipment

For keeping the boundary losses as small as possible the measuring vessel, a hollow glass sphere, 34 cm in diameter and with 1.3 mm wall thickness, is suspended by thin steel wires in a container which can be evacuated. The vessel is excited electrostatically with the aid of a wide annular electrode and the oscillation is detected by an ADP crystal cemented to the wall, its output after amplification being recorded by a Neumann recorder to a logarithmic scale (Fig. 1). For selecting with certainty the same definite mode of oscillation for different liquids with somewhat shifted resonant frequencies, a very slow registration of the frequency response within

a small range is made, from which the very sharp resonances (having half-widths of 0.3–0.7 c/s) may be recognised from their beats with the exciting frequency.

### c) Reverberation method

#### $\alpha$ ) Principle of the method

The method used for the present work has been developed by MEYER and SKUDRZYK [23], [22] following the principle of the two chamber reverberation method of KNUDSEN [42] and improved by the authors [37] and by MULDER [25]. A vessel of low degree of symmetry filled with the liquid to be investigated is excited by a frequency band to a large number of normal modes of oscillation so that a diffuse sound field occurs. If the normal modes are nearly uniformly influenced by the boundary losses, an approximately exponential decay of the sound energy results, the decay constant of which is partly due to the medium and partly due to the effect of the walls:  $\delta = \alpha c + A/R + B/h$  where  $A = \text{const}$ ,  $B = B(R)$ . The second part can be eliminated either by altering the depth  $h$  of the water and the dimensions (radius  $R$  and height  $H = 2R$ ) of the vessel and by extrapolating to an infinitely large vessel,—this method is employed in the case of pure water—or by comparing the decay constant with that found for a standard liquid. In the case of aqueous solutions of electrolytes, pure water ( $\alpha/v^2 = 25 \cdot 10^{-15} \text{ s}^2/\text{m}$ ) is employed for comparison. This can be done under the supposition that the boundary losses are unaltered when the liquid is replaced by the standard liquid, i.e. that the increase of friction at the wall, due to the higher viscosity of the electrolyte solution, is of vanishing influence compared with the increase of losses in the liquid. This supposition is fulfilled in all cases of solutions with measurable absorption.

#### $\beta$ ) Measuring apparatus<sup>3</sup>

The reverberation vessel, a seamless cylindrical 100 litres vessel (54 cm in diameter and in height) made of pure anodised and varnished aluminium (3.5 mm thick) is suspended somewhat inclined from 3 points on its upper rim by means of steel wires, on each of which three steel spheres are pressed, avoiding a transmission of sound energy, as suggested by MEYER and SKUDRZYK [23]. The two larger vessels (75 and 105 cm in diameter), used for the two chamber method, are welded for technical reasons. For measuring liquids of high chemical activity a 90 litres glass vessel is used.

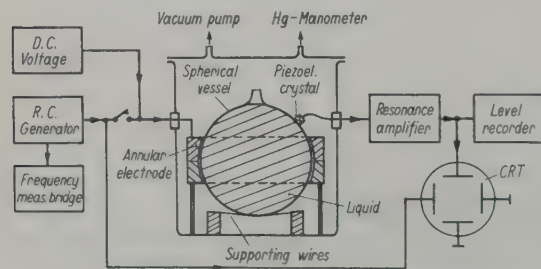


Fig. 1. Block diagram of the apparatus for measuring sound absorption, using single normal modes of oscillation of the liquid in a spherical vessel (frequency range 4–50 kc/s).

<sup>3</sup> The apparatus was built by Dr. H. HAAS.



The vessels are excited by means of an ADP- or a Rochelle salt-crystal ( $10 \times 10 \times 4 \text{ mm}^3$ ) cemented to the wall of the vessel using a little vaseline (Fig. 2). The frequency band for excitation (20 kc/s bandwidth) is generated by pulsing a variable carrier frequency which is restricted to 5 definite values, i.e. 50, 100, 200, 500, 1000 kc/s. The repetition rate of the pulses can

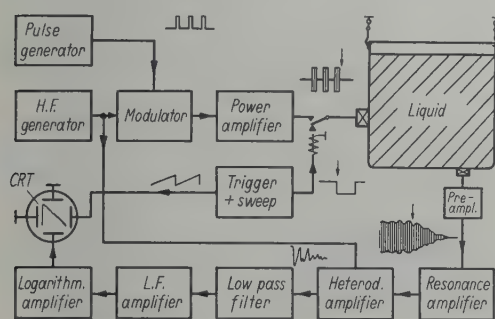


Fig. 2. Block diagram of the apparatus for measuring sound absorption, using the reverberation in a cylindrical vessel filled with the liquid (frequency range 50...1000 kc/s).

be altered between 5 and 50 p/s, to match it to the initial slope (50 dB/s for pure water at 100 kc/s) of the reverberation curves. The electric output of a piezoelectric receiver, pressed to the wall, is a measure of the sound energy in the vessel and is, after amplification, frequency conversion, and filtering, recorded by a Neumann type high speed level recorder or (for high decay rates) by a logarithmic amplifier combined with an oscilloscope.

#### d) Optical method; apparatus used in the frequency range 3...15 Mc/s

In this frequency range, the attenuations to be measured are larger than 3 dB/m, so that measurements can be carried through with progressive waves. For indication the optical method [43] was chosen because of the independence of transmitting and receiving set from each other. A sound beam, radiated by a quartz crystal, is sent into the measuring vessel (1 m in length) the side walls of which are made of glass. To avoid standing waves, the sound is absorbed by rubber wedges at the end of the vessel. The optical arrangement can be seen from Fig. 3. The sound beam is crossed perpendicularly by a parallel beam of light, which, by moving the mirrors, can be shifted along it. The first order of the resulting diffraction pattern is given to a photoelectric cell, followed by a multiplier, and the electric output recorded by a logarithmic level recorder. The sound is modulated and the multiplier tuned to

the modulation frequency by an LC-circuit. Thus scattered light does not disturb the measurements. The attenuation of the solution to be measured results from the slope of the straight line drawn by the level recorder when the mirrors are moved along the sound beam. The measuring accuracy amounts to about 5%.

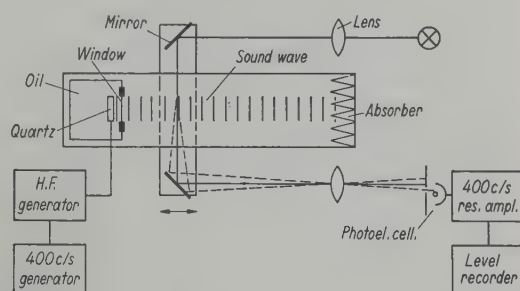


Fig. 3. Block diagram of the apparatus for measuring sound absorption in progressive waves, using the optical method (frequency range 3...15 Mc/s).

#### e) Optical method; apparatus used in the frequency range 20...100 Mc/s

The principle of the method used in this frequency range is the same as in the range 3...15 Mc/s, with the only difference that in this case the vessel is moved instead of the light beam [40]. The quartz crystal (9.2 Mc/s) is fixed in the bottom of the measuring vessel and radiates perpendicular to the surface (Fig. 4). The

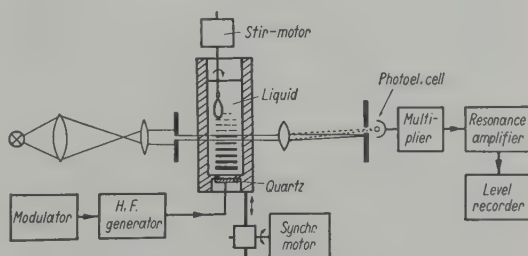


Fig. 4. Block diagram of the apparatus for measuring sound absorption in progressive waves, using the optical method (frequency range 20...100 Mc/s).

maximum measuring distance amounts to 50 mm. It is difficult in this frequency range to generate a diffraction pattern, if the direction of the incoming light is exactly parallel to the wavefront of the sound, but a relatively bright first diffraction order is observed on one side of the zero order if the angle of incidence is only slightly altered. An attempt to use this unsymmetrical diffraction pattern for the measurements yielded an exactly exponential decay with distance in a

ratio 300:1. As moreover absorption measurements with pure water proved to agree with the expected values within 5%, all measurements were made in this way. To avoid a splitting of the sound beam which occurs due to temperature gradients in the stationary liquid, the solution was stirred during the measurements.

#### 4. Preparation of the solutions

For measurements with pure water as well as for the aqueous solutions commercially obtained distilled water was employed. It is manufactured by the usual process, i.e. by distillation in an iron boiler followed by condensation in a copper cooling spiral. The degree of purity thus obtained seemed to be sufficient for the measurements.

The purity of the applied chemicals was an economic question. As for the reverberation measurements large quantities (100 litres) of the solution are necessary, no p.a.-substances (pro analysi) were employed, but the degree of purity "reinst" from MERCK and "chemisch rein" from RIEDEL DE HAEN. In the case of the optical measurements p.a.-chemicals have been used exclusively. In order to be independent of the water contents of the salts, concentrated salt solutions were prepared, the concentration of which was determined by exact density measurements using an areometer. These highly concentrated solutions were diluted quantitatively with pure degassed water to the required concentration.

For eliminating dust particles from the air and suspended particles, which were present in the distilled water and which, in addition, were brought into the solutions by the salts, the solutions as well as the pure water were filtered before the measurements.

From the measurements it became clear that dissolved air scarcely influences the damping in water, but that air-bubbles or air-films, the appearance of which is caused by temperature or pressure variations, very much disturb particularly the measurements with the resonance and reverberation methods. The water therefore was degassed before use with the aid of a water jet pump. While water which has been standing in the open air contains about 3 cm<sup>3</sup> air per litre, the air contents after the degassing were in most cases less than 1 cm<sup>3</sup>/litre.

As for the measurements of the temperature dependence no thermostat of the required size (about 1 m<sup>3</sup>) was available, the measuring liquid was heated by an immersion heater and the temperature dependence taken during the slow cooling.

### 5. Results of measurements

#### a) Results of absorption measurements in pure water

To determine the absolute value of the absorption of pure water, a series of measurements was carried out with the reverberation method for decreasing water level in three measuring vessels. After every 2...5 mm fall of the water level, the reverberation curve was recorded at three measuring frequencies 50, 100 and 200 kc/s. From the slope of the plot of the product "decay constant  $\times$  height" vs. height (for the 105 cm vessel given in Fig. 5a) the decay constant in an infinitely long cylinder ( $\delta^+ = 9.2, 14.2$  and 29 dB/s) can be taken. The extrapolation to an infinitely

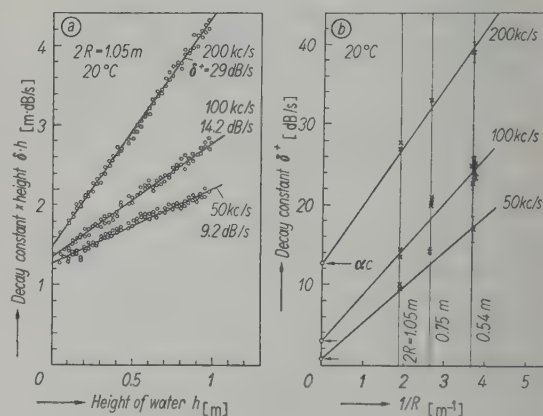


Fig. 5. Measurements of the absorption of pure water.

- Decay constant  $\times$  height ( $\delta \cdot h$ ) against height of water ( $h$ ) at 200 kc/s in a cylindrical aluminium vessel (105 cm  $\varnothing$ ) with pure water. The slopes of the straight lines yield the decay constants for infinite height ( $\delta^+$ ).
- Decay constant ( $\delta^+$ ) of pure water (extrapolated to infinite height of water) against the reciprocal of the radii of the vessels ( $1/R$ ) for three different frequencies.

wide cylinder (free medium) is made by plotting these values against the reciprocal of the radius ( $1/R$ ) which must give straight lines intercepting the ordinate axis ( $1/R=0$ ) at  $\alpha_c$ . In Fig. 5b the straight lines are drawn corresponding to the value  $\alpha/\nu^2 = 25 \cdot 10^{-15} \text{ s}^2/\text{m}$ , as often determined for higher frequencies. Taking into account a smaller importance of the values in the 75 cm vessel, their deviation probably being due to a welded seam somewhat worse, the scatter of the measuring points gives an uncertainty in the determination of  $2\alpha/\nu^2$  (marked in Fig. 6) which increases rapidly with decreasing frequency.

The results agree within the limits of measuring accuracy with earlier measurements of MEYER and SKUDRZYK [23] (at 14°C), if these are cor-



rected with respect to temperature. The new results do not, however, allow a decision to be made as to the presence of a 20% increase in  $2\alpha/\nu^2$  as was expected by KNESER [1] below 1 Mc/s (due to the heat of vibration). A summary of all recently published values for  $2\alpha/\nu^2$  of pure water (see Fig. 6) gives a good picture of the possible measuring accuracy and shows that the assumption of a value for  $2\alpha/\nu^2$  independent of frequency over the whole frequency range seems to be justified.

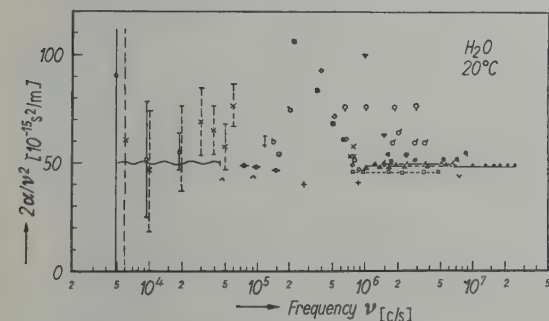


Fig. 6. ( $2\alpha/\nu^2$ ) of pure water against frequency (summary of all recently published values).

○ BAUMGARDT (1936)	▲ HSU (1945)
× BIAQUARD (1936)	▼ TEETER (1946)
• CLAEYS, ERRERA, SACK (1937)	● RAPUANO (1947)
+ FOX (1937)	◀ PINKERTON (1947)
• BXR (1937)	▼ LABOW, WILLIAMS (1947)
■ BUSS (1938)	* SMITH, BEYER (1948)
✓ BAZULIN (1938)	• MULDER (1948)
✓ GROBE (1938)	▲ LIEBERMANN (1948)
◊ WILLARD (1941)	• LEONARD (1948)
• FOX, ROCK (1941/46)	• ITTERBEEK, SLOOTMAKERS (1949)
• RÜFER (1942)	• TALL (1950)
• MEYER, SKUDRZYK (1943)	

The measurements could not all be carried out at the same temperature, i.e. at 20°C, because it was difficult to maintain the measuring rooms at this temperature throughout the duration of the experiments. The results for the decay constants (including the influence of the cylindrical wall) are therefore reduced to 20°C with the aid of the known temperature dependence of the shear viscosity of water (see e.g. HALL [4]). This is possible because on the one hand the wall friction provides the main part of the decay constant  $\delta^+$  and on the other hand the pressure viscosity (volume viscosity) has essentially the same temperature curve as the shear viscosity according to known measurements [16], [20], [21] and also according to the theory of HALL [4].

#### b) Measurements with aqueous solutions of electrolytes

##### α) The absorption cross-section of a molecule

By employing pure water for comparison, one obtains directly from a difference measurement

the absorption increase due to the presence of an electrolyte. This increase (the "electrolyte absorption") is not necessarily due only to sound-absorbing processes in which the constituents of the electrolyte themselves are taking part. It can also be caused by an alteration of the absorption of the solvent (i.e. of the water). For pure water it is known that very probably a structure relaxation is present on the exact nature of which different views are held. EUCKEN [7] suggests an alternate formation and dissociation of 8-molecule-aggregates. Through its hydration the dissolved electrolyte alters the structure equilibrium of the water and thereby changes its absorption. It is to be expected, however, that a considerable decrease in the absorption of the water occurs only for large concentrations of the electrolyte. By the above described "solvent effect" the absorption of the electrolyte molecules would, according to this conception, be partly compensated. The negative "solvent effect" cannot be greater than the water absorption itself and therefore is of no importance in the case of large electrolyte absorption. If the electrolyte absorption is, however, small compared with that of the water, as is sometimes the case at frequencies above 3 Mc/s, the electrolyte effect can be noticeably compensated by the "solvent effect". This is to be taken into account in considering the results, particularly when the measured absorption is referred to the number of electrolyte molecules per unit volume  $nL$  (where  $n$  is the concentration in moles per unit volume and  $L$  is the number of molecules per mole). The absorption effect of a single electrolyte molecule is then obtained in the form of an absorption cross-section  $Q$

$$Q = 2\alpha/(nL),$$

or

$$Q [\text{m}^2] = 1.66 \cdot 10^{-25} \times \frac{2\alpha [\text{cm}^{-1}]}{n [\text{moles/l}]}$$

if the usual units are employed. The absorption cross-section can be visualized as that cross-section area normal to the progression direction of a plane wave through which the energy which is absorbed by a single electrolyte molecule passes. The absorption cross-section is, however, a mean value over all molecules added to the solution, so that a part of the molecules can be in a state in which they are not directly taking part in the absorption. This part can alter with concentration and temperature. It follows that thus the absorption cross-section can alter with concentration.

For the recognition of relaxation processes (having a time constant  $\tau$ ) it is particularly useful

to plot the absorption coefficient divided by the frequency  $\nu$  (or multiplied by the wavelength  $\lambda$  resp.), because the relaxation curve is easy to recognise in this form. The normal notation

$$\alpha/\omega = \frac{A\omega}{1 + \omega^2\tau^2}$$

gives

$$\alpha \cdot \lambda = \frac{A' c \cdot \nu_m}{\nu_m/\nu + \nu/\nu_m}$$

where  $c$  is the velocity of sound and  $\nu_m = 1/2\pi\tau$ . In a double logarithmic representation the dependence of  $\alpha\lambda$  on the frequency results in a curve, being symmetrical with respect to the relaxation frequency  $\nu_m$  and having a linear increase ( $\sim \nu/\nu_m$ ) and a linear decrease ( $\sim \nu_m/\nu$ ); this type of representation can also be applied to the absorption cross-section. The value

$$Q\lambda = \frac{2\alpha\lambda}{nL}$$

is employed for the plotting of the experimental results; it can be visualized as follows:  $Q\lambda$  corresponds to the volume in a plane progressive sound wave which contains that amount of energy which is absorbed by a single molecule in one period.

### $\beta$ ) Error limits: relative accuracy

The absorption increase due to the electrolytes (electrolyte absorption) is determined by a difference measurement. The relative accuracy of the  $\alpha$ -values therefore decreases with decreasing electrolyte absorption. As this, in general, increases with increasing concentration, the relative accuracy of a  $Q\lambda$ -value is not only dependent on its absolute value, but also upon the concentration at which it was determined. This is to be taken account of in the evaluation of the  $Q$ - and  $Q\lambda$ -values.

In disagreement with former assumptions, most measurements showed a linear increase of the absorption with concentration, so that the absorption cross-section (Fig. 8) is independent of concentration up to about 0.1 moles/litre. Therefore, if  $Q\lambda$  is plotted against frequency, the resulting curves coincide. To increase the measuring accuracy, mean values have been taken in the case of most of the measuring points, given in the following chapter, over measurements at up to 10 different concentrations. Other than linear dependence of the absorption cross-section on concentration was observed only for a few salts and for sulphuric acid, for which the concentrations of the measured solutions are given in the figures.

### $\gamma$ ) Measuring results for aqueous solutions of electrolytes

In consideration of the great amount of time and material spent on an absorption measurement, it is hardly possible to carry out measurements for all interesting parameters with all the electrolytes which come into question. Thus measurements were confined to inorganic salts and series of measurements on the influence of definite quantities were partly carried out only in a few cases. Such series of measurements dealt with: (i) the influence of the valency of the constituents of an electrolyte, (ii) the dependence upon concentration, (iii) the frequency response, (iv) the influence of the addition of other electrolytes to the solution of a single electrolyte, (v) the influence of the pH-value of the solution, (vi) the dependence of the absorption upon temperature.

(i) The influence of the valency of the constituents of an electrolyte on the absorption.

1-1-valent electrolytes (e.g. NaCl, NaBr, KBr, KJ) in general cause no measurable electrolyte absorption, i.e. solutions of these electrolytes have no higher absorption than pure water. (The measuring accuracy amounts to about the order of magnitude of the absorption of water at low frequencies and about 5% of the absorption of water at high frequencies ( $> 10$  Mc/s).) At high frequencies "negative" electrolyte absorption could be observed with certainty. It is due to a structure-changing influence of the solute on the water. As an example, the concentration dependence of the absorption of an NaBr solution at two different frequencies is given in Fig. 7. In this case the absorption of the water is diminished to finally 70% of its original value. Similar properties are shown by NaJ.

2-1- and 3-1-valent electrolytes as well as 1-2-valent ones do not react considerably differently at the lower frequencies. They only show measurable absorption at frequencies above 10 Mc/s as is shown in Fig. 9 and 10.

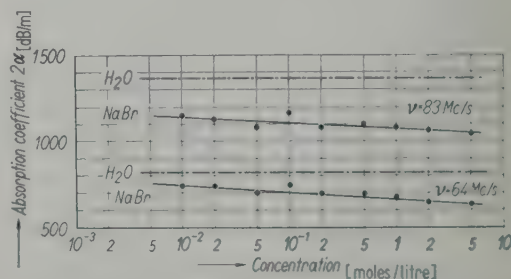


Fig. 7. Absorption coefficient ( $2\alpha$ ) of an NaBr-solution vs. concentration at 64 and 83 Mc/s. The dotted lines give the absorption coefficient for pure water.



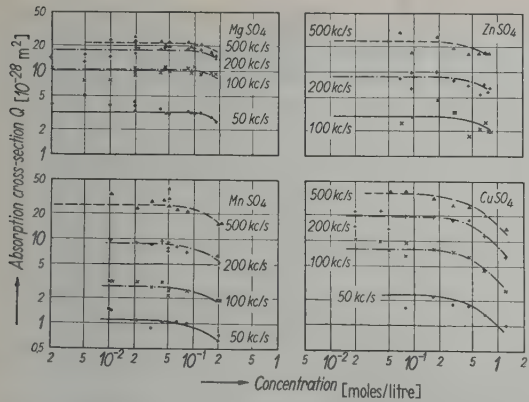


Fig. 8. Dependence of the absorption cross-section ( $Q$ ) of  $MgSO_4$ ,  $MnSO_4$ ,  $ZnSO_4$  and  $CuSO_4$  on concentration.

2-2-valent electrolytes on the other hand generally have a considerable electrolyte absorption in the whole frequency range in question. No exceptions have been found. The salts under experiment were mainly sulphates, such as  $BeSO_4$ ,  $NiSO_4$ ,  $MgSO_4$ ,  $CoSO_4$ ,  $MnSO_4$ ,  $ZnSO_4$ ,  $CuSO_4$ . It is difficult to find apart from sulphuric acid other inorganic bivalent acids whose salts with bivalent metals or radicals not only dissolve in water, but can also be obtained with a sufficient degree of purity in the necessary quantities. Thiosulphates, chromates, molybdates and wolframates come into question.  $MgS_2O_3$ ,  $MgCrO_4$  and  $CaCrO_4$  have been investigated, having a considerable absorption, too.

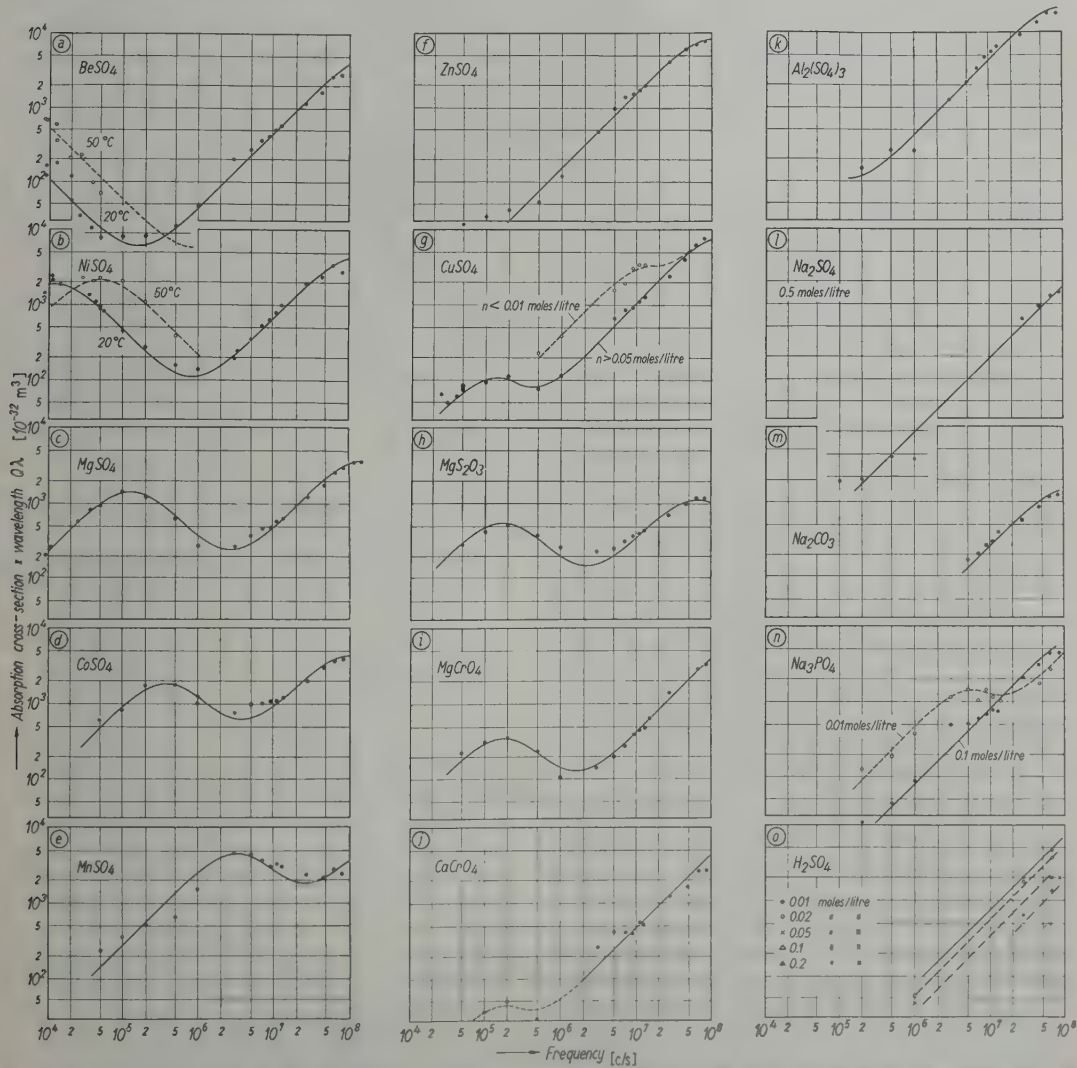


Fig. 9. Frequency response of the absorption cross-section  $\times$  wavelength ( $Q\lambda$ ) at  $20^\circ C$  for some of the electrolytes investigated. (Where no concentrations are given, independence of the absorption cross-section of concentration has been observed and the given values are mean values over measurements at different concentrations.)

As a 3-2-valent electrolyte,  $\text{Al}_2(\text{SO}_4)_3$  has been investigated. This salt has the largest maximum value of  $Q \cdot \lambda$  of all salts which have been under experiment.

(ii) The dependence of the absorption upon concentration.

For nearly all 2-2-valent electrolytes investigated, the results of the measurements agree with a linear dependence of the electrolyte absorption on concentration within the limits of measuring accuracy from concentrations of about 0.001 to 0.1 mole/litre. The absorption cross-section therefore is independent of the concentration in this range. Some examples are given in Fig. 8. At higher concentrations, the absorption cross-section steadily decreases with increasing concentration. Exceptions only occur with salts like  $\text{Na}_3\text{PO}_4$ , where the percentage of the different ions  $\text{Na}^+$ ,  $\text{Na}_2\text{PO}_4^-$ ,  $\text{NaPO}_4^{2-}$  and  $\text{PO}_4^{3-}$  present in the solution is assumed to vary with concentration.

(iii) The frequency response of the absorption of electrolyte solutions.

All electrolytic solutions which showed a measurable absorption in any frequency range have been investigated with respect to the frequency response of this absorption. The results are given in Fig. 9a...o in which the absorption cross-section is plotted against frequency in a double logarithmic scale. All frequency response curves show the typical shape of relaxation curves, or consist of an addition of several relaxation curves. To give a better survey and to simplify comparison all curves without the measuring points are given together in Fig. 10a. The same results are given in Fig. 10b once more, but here, instead of  $Q\lambda$ ,  $\alpha/\nu^2$  is plotted against frequency. This kind of representation, which shows the above mentioned steps at the relaxation frequencies, gives a better impression of the real amount of the absorption of 0.1 mole/litre solutions compared with the absorption of pure water.

(iv) The influence of the addition of other electrolytes to the solution of a single electrolyte.

The investigation of synthetic sea-water (0.454 moles/litre  $\text{Na}^+$ , 0.010  $\text{K}^+$ , 0.052  $\text{Mg}^{++}$ , 0.010  $\text{Ca}^{++}$  and 0.530  $\text{Cl}^-$ , 0.001  $\text{Br}^-$ , 0.0275  $\text{SO}_4^{--}$ , 0.0025  $\text{CO}_3^{--}$ ) yielded an absorption, which is equal to that of a pure  $\text{MgSO}_4$  solution of 0.014 moles/litre. This "equivalent" concentration is smaller than that of the  $\text{Mg}^{++}$  or  $\text{SO}_4^{--}$  ions. The result is in good agreement with measurements of other authors as can be seen from Fig. 11.

For further investigation of the influence of one electrolyte on the other, increasing amounts of  $\text{NaCl}$  have been added to  $\text{MgSO}_4$  solutions of different concentrations. The result can be given in an empirical mixing rule which gives the reduction in the efficiency of the  $\text{MgSO}_4$  con-

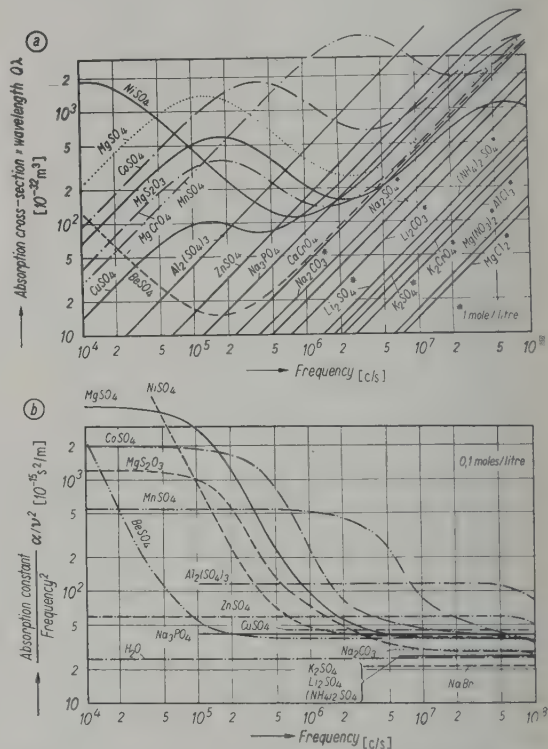


Fig. 10a. Summary of all measured frequency response curves (without measuring points) (\* concentration 1 mole/litre).

Fig. 10b.  $\alpha/\nu^2$  for 0.1 mole/litre solutions of some electrolyte solutions plotted against frequency (calculated from Fig. 10a).

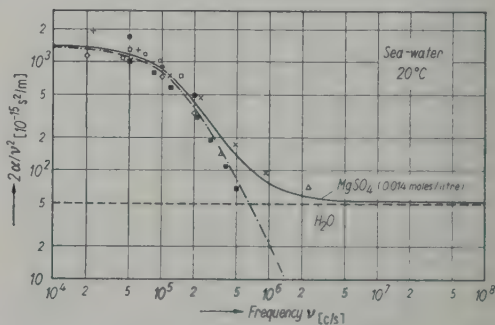


Fig. 11.  $2\alpha/\nu^2$  of sea-water as a function of frequency (summary of published values).

- ◇ EVEREST, O'NEIL (1946)
- + UNIVERSITY OF CALIFORNIA (1947)
- △ THIESSEN, LESLIE, SIMPSON (1948)
- × LIEBERMANN (1948)
- LEONARD (natural) (1949)
- LEONARD (synth.) (1949)
- TAMM (synth.) (1950)



centration. By assuming a linear relationship between concentration and absorption ( $\alpha_0$ ) of  $\text{MgSO}_4$ , the decrease in absorption to the value ( $\alpha$ ) can be considered as an apparent reduction of the  $\text{MgSO}_4$  concentration to an effective concentration  $[\text{MgSO}_4]_{\text{eff}}$ . The empirical mixing rule (which will be explained later) is then

$$\frac{\alpha}{\alpha_0} = \frac{[\text{MgSO}_4]_{\text{eff}}}{[\text{MgSO}_4]} = \frac{[\text{MgSO}_4]}{[\text{MgSO}_4] + f \cdot [\text{NaCl}]}; f = 1/5,$$

which may also be written in the form

$$\frac{\Delta\alpha}{\alpha} = \frac{\alpha_0 - \alpha}{\alpha} = \frac{[\text{NaCl}]}{[\text{MgSO}_4]} \cdot f,$$

in which it can be easily checked by the experimental results. In Fig. 12 three series of measurements with different concentrations of  $\text{MgSO}_4$  are plotted to a double logarithmic scale, yielding a straight line with a slope of  $45^\circ$  (thus proving the linearity of the mixing rule) and a factor  $f=0.21$ . Further on, Fig. 12 shows the results of similar measurements with  $\text{MnSO}_4$  and  $\text{NaCl}$ , in this case yielding a factor  $f=0.08$ .

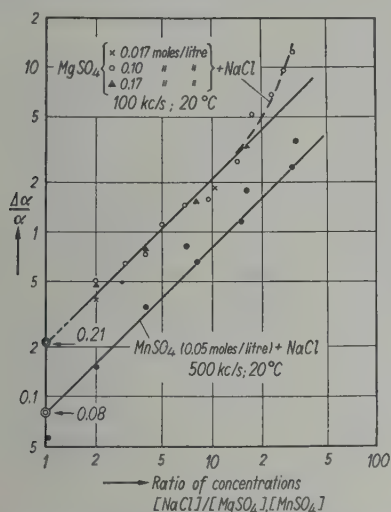


Fig. 12. Relative decrease of absorption  $\Delta\alpha/\alpha$  (referred to the absorption of the mixture) of aqueous solutions of  $\text{MgSO}_4$  and  $\text{MnSO}_4$  when adding  $\text{NaCl}$ , plotted against the ratio of the concentrations.

To study the influence of  $\text{Na}^+$  and  $\text{Cl}^-$  ions on  $\text{MgSO}_4$  solutions separately,  $\text{Na}_2\text{SO}_4$  or  $\text{MgCl}_2$  have been added to a 0.01 mole/litre  $\text{MgSO}_4$  solution. The result can be seen from Fig. 13. The absorption caused by the relaxation process, the relaxation frequency of which is 130 kc/s, is nearly doubled by addition of 0.01 mole/litre  $\text{Na}_2\text{SO}_4$  as well as by addition of 0.01 mole/litre  $\text{MgCl}_2$ . Further addition of  $\text{Na}_2\text{SO}_4$  or  $\text{MgCl}_2$  respectively only slightly enlarges the absorption

until a limiting value is reached which is about twice the original value. If the same measurements are made with a concentration of 0.04 mole/litre  $\text{MgSO}_4$ , the increase of absorption in both cases only amounts to about 20% of the  $\text{MgSO}_4$ -absorption.

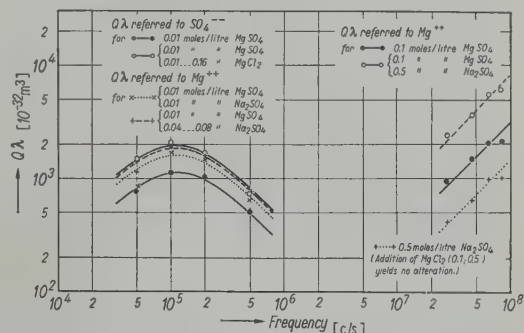


Fig. 13. Frequency response of the absorption cross-section  $\times$  wavelength ( $Q\lambda$ ) of mixtures  $\text{MgSO}_4 + \text{Na}_2\text{SO}_4$  and  $\text{MgSO}_4 + \text{MgCl}_2$ .

At frequencies above 3 Mc/s a mere addition of the absorptions of the components is observed.  $\text{MgCl}_2$ , which causes no measurable absorption in this frequency range, causes no change in the  $\text{MgSO}_4$ -absorption, and the absorption of  $\text{Na}_2\text{SO}_4$ , also given in Fig. 13, adds to that of  $\text{MgSO}_4$ . Further, mixtures of two bivalent sulphates have been investigated by measuring 0.01  $\text{MgSO}_4 + 0.01$   $\text{MnSO}_4$  the relaxation frequencies of which are close together, and 0.025  $\text{BeSO}_4 + 0.025$   $\text{MnSO}_4$  with relaxation frequencies far apart from each other. In both these cases an addition of the absorption was observed in the whole frequency range.

(v) Dependence of the absorption on the hydrogen-ion concentration of the solutions.

The influence of the pH-value of the solutions has been investigated by adding alkali ( $\text{NaOH}$ ) or acid ( $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ ) to solutions of  $\text{MgSO}_4$  and  $\text{MgCl}_2$ . The results can be seen from Fig. 14. In general the absorption decreases with increasing concentration of the hydrogen-ions, while the relaxation frequency seems to be slightly shifted to higher frequencies (Fig. 15). Remarkable is the fact that  $\text{MgCl}_2$ , which shows no electrolyte absorption in neutral solution, shows an absorption comparable to that of  $\text{MgSO}_4$  in the vicinity of the lower maximum, if  $\text{NaOH}$  is added. Unfortunately these measurements can only be made with very low concentrations, to prevent  $\text{Mg}(\text{OH})_2$  from falling out. Thus the measuring accuracy is too low to decide whether the relaxation frequency of this absorption process is the same as in the case of  $\text{MgSO}_4$  or not.

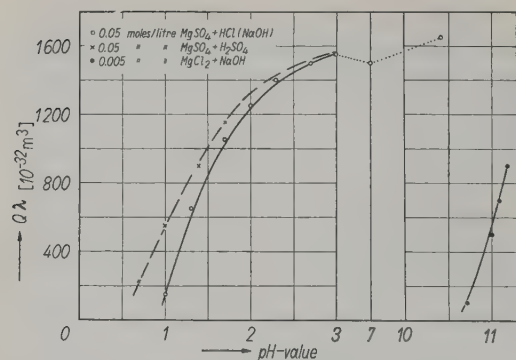


Fig. 14. Absorption cross-section  $\times$  wavelength ( $Q\lambda$ ) of  $\text{MgSO}_4$  and  $\text{MgCl}_2$  solutions in dependence on the hydrogen ion concentration.

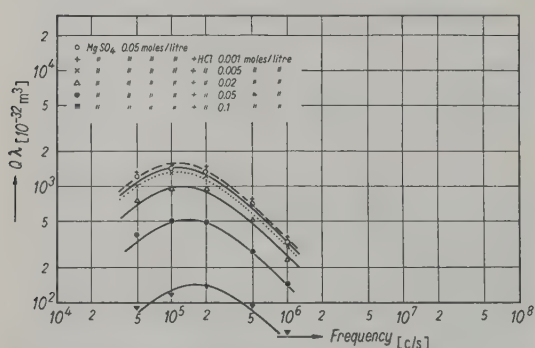


Fig. 15. Frequency response of the absorption cross-section  $\times$  wavelength ( $Q\lambda$ ) of mixtures  $\text{MgSO}_4 + \text{HCl}$ .

(vi) The dependence of the absorption upon temperature.

The temperature dependence of the absorption has been investigated exactly at a 0.05 mole/litre  $\text{MgSO}_4$ -solution (Fig. 16a). With increasing temperature the relaxation curves are shifted to higher frequencies, the amount of maximum absorption remaining nearly unchanged. The experimental activation energy of the relaxation process obtained from the shift of the relaxation frequency amounts to about 6.5 kcal/mole for  $\text{MgSO}_4$ . This value has been calculated from the slope of the curve  $\log(\nu_m/T)$  vs.  $1/T$  (Fig. 16b) because of the linear relationship between these two quantities (see 6, b). Similar measurements have been made for  $\text{NiSO}_4$  and  $\text{CoSO}_4$ . The resulting experimental activation energies are: 8.6 kcal/mole for  $\text{NiSO}_4$  and about 6 kcal/mole for  $\text{CoSO}_4$ . For temperatures above 60°C difficulties arise in the measurements so that the corresponding points are somewhat less accurate. WILSON [3] gives a somewhat higher experimental activation energy for  $\text{MgSO}_4$ , but only two of his seven measuring points (35 and 42°C) do not coincide with our measurements.

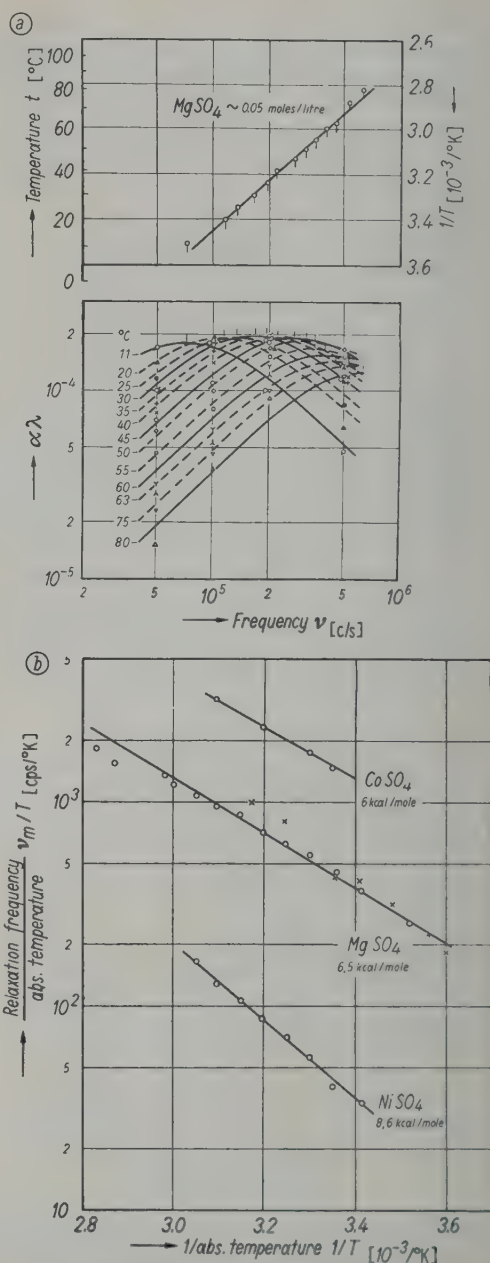


Fig. 16. Temperature dependence of the relaxation frequency.

(a) Relaxation curves ( $Q\lambda$  vs. frequency) of  $\text{MgSO}_4$  and their relaxation frequencies  $\nu_m$  for different temperatures.

(b)  $\nu_m/T$  vs.  $1/T$  for  $\text{CoSO}_4$ ,  $\text{MgSO}_4$  and  $\text{NiSO}_4$ . The slopes of the straight lines yield the experimental activation energies ( $\times$  measured by WILSON [3]).

The steady increase of the curves (above 10 Mc/s) is also shifted to higher frequencies with increasing temperature, but since the maximum is above the measuring frequency range, no



activation energy can be determined from the temperature dependence.

The fact that the curves are shifted with temperature without a change in the maximum of the value  $Q\lambda$  allows conclusions with respect to the shape of the frequency response curves below the lowest measuring frequency. A measurement for  $\text{NiSO}_4$ , with 10 kc/s at 50°C e.g. corresponds to 2 kc/s at 20°C. For other substances this relation is slightly changed because of their different activation energies. With this method (Fig. 9a), the relaxation frequency of  $\text{BeSO}_4$  could be estimated to be lower than 1 kc/s at 20°C. In the case of  $\text{NiSO}_4$ , the relaxation frequency of which is 10 kc/s, the decrease of the relaxation curve to lower frequencies could be measured at 50°C (Fig. 9b).

#### δ) Summary of the results

1. Concentration independency of the absorption cross-section.

2. Dependence of the absorption cross-section on the valency of both ions.

3. Steady increase of  $Q\lambda$  towards high frequencies.

4. Additional relaxation maximum at 2-2-valent salts

a) Concentration independency of the relaxation frequency.

b) Dependency of the relaxation frequency on the cation:

$\text{BeSO}_4$	$< 10^3$ c/s	$\text{CoSO}_4$	$4 \cdot 10^5$ c/s
$\text{NiSO}_4$	$10^4$ c/s	$\text{MnSO}_4$	$3 \cdot 10^6$ c/s
$\text{MgSO}_4$	$1.3 \cdot 10^5$ c/s	$\text{ZnSO}_4$	$> 10^8$ c/s
$\text{MgS}_2\text{O}_3$	$1.8 \cdot 10^5$ c/s	$\text{CuSO}_4$	$> 10^8$ c/s
$\text{MgCrO}_4$	$1.8 \cdot 10^5$ c/s		

c) Temperature shift of the relaxation frequencies to higher frequencies with increasing temperature.

5. Influence of the addition of other electrolytes:

Substances	Relaxation maximum	Steady increase
$\text{MgSO}_4$ ( $\text{MnSO}_4$ ) + NaCl	decrease	decrease
$\text{MgSO}_4$ + $\text{MgCl}_2$	limited increase	addition
$\text{MgSO}_4$ + $\text{Na}_2\text{SO}_4$	limited increase	addition
2-valent sulphate + 2-val. sulphate	addition	addition

6. Decrease of the absorption with increasing hydrogen-ion concentration.

#### 6. Discussion of the results

In every case the measured frequency response of the absorption agrees with that of a relaxation

process or a superposition of several relaxation processes, the corresponding relaxation frequencies of which, however, often must be assumed higher than 100 Mc/s, and could not be determined therefore.

#### a) Thermal relaxations

As the origin of this relaxation absorption we may first think of thermal relaxations by the excitation of molecular degrees of freedom. Such relaxations can be expected only in the case of ions consisting of more than one atom, as there are  $\text{SO}_4^{--}$ ,  $\text{S}_2\text{O}_3^{--}$ ,  $\text{CO}_3^{--}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , etc. This kind of process cannot be responsible for the additional relaxation maximum of the 2-2-valent electrolytes, which only occurs if both ions are present. The steady increase of the absorption towards high frequencies, however, might possibly be caused by such processes, since e.g. the  $\text{SO}_4^{--}$  ion shows its brightest Raman-line at a wave number  $\Delta n = 980 \text{ cm}^{-1}$ , corresponding to an energy of about 2.8 kcal/mole. From this energy value a relaxation frequency somewhat higher than 100 Mc/s can be expected. This explanation agrees with the constancy of the absorption cross-section, since the probability for the excitation of molecular degrees of freedom does not depend on concentration. It is in contradiction to the decrease of the absorption cross-section with concentration observed in the case of  $\text{H}_2\text{SO}_4$  (Fig. 9o), which, however, can be explained by the formation of  $\text{HSO}_4^-$  ions, whose Raman lines are somewhat shifted. The decrease in absorption with increasing concentration agrees with the decrease of the percentage of  $\text{SO}_4^{--}$  ions, calculated from the comparatively low dissociation constant  $K = 10^{-2}$  of the second step of the dissociation of  $\text{H}_2\text{SO}_4$ . The decrease of the absorption of bivalent sulphates when NaCl is added might be explained analogously. The other anions mentioned above show similar Raman lines, but no correspondence can be observed between the intensity of the lines and the amount of the absorption. The  $\text{NO}_3^-$ -ion for instance has the brightest Raman-lines but the smallest absorption cross-section.

#### b) Structural relaxations

Another possibility to explain the absorption is the assumption of structural relaxations. Two kinds of structural relaxations, the hydration and the ion association may be discussed here.

The hydration of the ions, i.e. the formation of hydrate shells around the ions in the solution, caused by electrostatic forces, occurs as a first order reaction and therefore does not depend on



concentration as long as a sufficient number of  $\text{H}_2\text{O}$  molecules is available. The activation energy  $\Delta F_2^+$  of the water molecules in the hydrate shells determines a corresponding relaxation frequency  $\nu_m = 1/2\pi\tau$  for each sort of ions, given by the wellknown formula

$$\begin{aligned} 1/\tau &= k_1 + k_2 = \frac{kT}{h} \cdot e^{-\left(\Delta F_2^+/RT\right)} [e^{-\Delta F/RT} + 1] \approx \\ &\approx \frac{kT}{h} \cdot e^{-\left(\Delta F_2^+/RT\right)} \end{aligned}$$

where  $k_1$  and  $k_2$  are the reaction rates in both directions ( $k_2 > k_1$ ),  $k$  BOLTZMANN's constant,  $T$  the absolute temperature,  $h$  PLANCK's constant,  $R$  the gas constant per mole, and  $\Delta F = \Delta F_2^+ - \Delta F_1^+$ . Thus the relaxation frequency should decrease with increasing valency and with decreasing diameter of the ions, in agreement with the observations at the additional relaxation maximum of the bivalent sulphates. The fact, that  $\text{MgSO}_4$ ,  $\text{MgCrO}_4$  and  $\text{MgS}_2\text{O}_3$  show nearly the same relaxation maximum, seems to confirm this assumption; the fact, however, that  $\text{MgCl}_2$  shows no absorption, and the increase of absorption, observed, when  $\text{Na}_2\text{SO}_4$  is added to an  $\text{MgSO}_4$ -solution, contradicts it.

The influence of both ion partners to the absorption in a solution of a single electrolyte and that of univalent ions in mixtures with 2-2-valent electrolytes leads to the assumption of an interaction between the ions. There are several different possibilities of ionic interaction, which should be connected with a relaxation process: The dissociation (as  $\text{MgSO}_4 \rightleftharpoons \text{Mg}^{++} + \text{SO}_4^{--}$ ) which was first assumed by LIEBERMANN [8] to be the origin of the relaxation absorption of  $\text{MgSO}_4$  solutions, is a reaction of higher order than first, which normally yield no concentration independence of absorption cross-section and relaxation frequency at the same time. At sufficiently low concentration (high dissociation) the relaxation frequency should be independent of concentration while the absorption cross-section should be proportional to the percentage of the undissociated molecules, or more accurately proportional to the product concentration  $\times$  square of the activity coefficient. In the case of high concentration (low dissociation) both quantities should depend on concentration. In the case of bivalent sulphates, however, (especially for  $\text{MgSO}_4$ ) a nearly constant degree of dissociation can be derived from the concentration dependence of the activity coefficient in a certain range (0.01–0.1 mole/litre). This really yields a concentration independence of absorption cross-section and relaxation frequency (see 6 c).

Certain effects in physical chemistry lead to the assumption of ion association, i.e. the association of anion and cation, each of them surrounded by its hydrate shell, to an ion pair (ion dipole). The equilibrium: ion pair  $\rightleftharpoons$  anion + cation obeys the law of mass action if the activity coefficients are taken into account. The assumption that this second order reaction should be responsible for the electrolyte absorption would therefore yield similar concentration dependences of absorption and relaxation frequency as the dissociation of molecules. The experimental results, however, require a reaction of the first order for their explanation, as would be given by the transition between two states of association of the ion pairs, differing by their energy levels. The different energy levels may result from a different arrangement of the hydrate water molecules between the two ions of an ionic dipole. Ion associates of this kind were assumed by BJERRUM [45], but he obtained from his theory only a low degree of association which therefore depends on concentration. An extremely high degree of association, as must be assumed here, could be made plausible from the anomalies with respect to the DEBYE-HÜCKEL theory observed with the conductivity of solutions of 2-2-valent electrolytes. If the degree of association is estimated from the difference in conductivity against infinitely diluted solutions, it varies from 30 to 70 % within the concentration range 0.001–0.1 mole/litre. The number of ion dipoles may be even more independent of concentration, since at high concentrations a part of the ions may be associated to quadrupoles or to still larger associates with relaxation effects which considerably differ from those of the dipoles.

Due to the smaller charge of the latter associates of bivalent with univalent ions should be less numerous, while associates of two univalent ions practically should not occur at all. This is in agreement with the measured valency dependence of the absorption cross-section [see 5, b,  $\delta$ , (2)].

With these assumptions the influence of the addition of other electrolytes in mixtures [5, b,  $\delta$ , (5)] too can be easily explained as far as the additional relaxation maximum is concerned. If e.g.  $\text{NaCl}$  is added to an  $\text{MgSO}_4$  solution, the number of  $\text{Mg-SO}_4$  associates is reduced in favour of  $\text{Mg-Cl}^+$  and  $\text{Na-SO}_4^-$  associates, the percentage of which is determined by the ion strengths of the partners. This explains quantitatively the mixing rule given above. Addition of  $\text{MgCl}_2$  to  $\text{MgSO}_4$  can increase the number of  $\text{Mg-SO}_4$  associates finally to the total number of  $\text{SO}_4^{--}$  ions



present, thus explaining the limited increase of the absorption cross-section. The same is valid vice versa in the case of mixtures of  $\text{MgSO}_4$  with  $\text{Na}_2\text{SO}_4$ .

The energy levels of the associates and therefore the relaxation frequencies are independent of concentration [5, b,  $\delta$ , (4a)] but depend on the diameter of the ions involved, thus yielding the succession of the relaxation frequencies of the different sulphates [5, b,  $\delta$ , (4b)].

With the assumption of ion pairs causing a relaxation absorption, only one relaxation maximum can be explained, so that the second increase of the absorption cross-section, observed in the case of the 2-2-valent salts must be due to another process, to the above mentioned thermal relaxations for instance. Difficulties however arise in explaining the increase of the absorption of  $\text{MgSO}_4$  solutions when alkali is added and the absorption measured with the mixture  $\text{MgCl}_2 + \text{NaOH}$ .

#### c) Chemical relaxations

As a third process, possibly causing a relaxation absorption, a chemical relaxation process may be discussed here. WILSON [3] mentioned the hydrolysis reaction as a possibility, but, as he believed, the results of absorption measurements with sea-water were in contradiction to this assumption. An improved model of this kind, however, allows the explanation of all results of absorption measurements in electrolyte solutions known up to now. The measuring results got with mixtures  $\text{MgCl}_2 + \text{NaOH}$  (absorption in the vicinity of the lower  $\text{MgSO}_4$ -maximum but no absorption at higher frequencies) and the influence of the pH-value of the solution show, that the dissociation reaction  $\text{MgOH}^+ \rightarrow \text{Mg}^{++} + \text{OH}^-$  really can be responsible for the absorption process which in this case has a relaxation frequency at about 130 kc/s.

On the other hand  $\text{H}_2\text{SO}_4$  shows an increase of  $Q\lambda$  towards high frequencies which is of the same order of magnitude as the second increase of the bivalent sulphate solutions (as  $\text{MgSO}_4$ ) so that this second increase might be ascribed to the dissociation of  $\text{HSO}_4^- \rightleftharpoons \text{H}^+ + \text{SO}_4^{--}$ .

The hydrolytic effect especially in  $\text{MgSO}_4$  solutions is of course very low. Moreover this normal hydrolysis cannot be responsible for the absorption since then the addition of e.g.  $\text{HCl}$  to a bivalent sulphate solution should yield a decrease of the absorption at the lower maximum (reduced concentration of  $\text{OH}^-$  and  $\text{MgOH}^+$ ) and an increase at higher frequencies (enlarged concentration of  $\text{H}^+$  and  $\text{HSO}_4^-$ ), while a decrease is observed in both parts of the curve.

From recent publications [46] it is known that  $\text{MgSO}_4$  and similar salts are not completely dissociated and that their degree of dissociation (about 10% undissociated) keeps constant at least in the concentration range 0.01...0.1 mole/litre. This constancy is due to a decrease of the activity coefficients proportional to  $1/\sqrt{c}$  in this range and might very well explain the observed concentration independence of the absorption cross-section if the dissociation-reaction is made responsible for the absorption.

Both processes (hydrolysis and dissociation reaction), each explaining only a part of the results, can be combined by assuming that the percentage of hydrolysis products is determined by the number of undissociated molecules. This can be done by postulating the dissociation reaction occurring in steps which e.g. may be the following ones:

- 1)  $\text{MgSO}_4 \cdot \text{H}_2\text{O}$
- 2)  $\text{MgOH}^+ + \text{HSO}_4^-$
- 3)  $\text{MgOH}^+ + \text{H}^+ + \text{SO}_4^{--}$
- 4)  $\text{Mg}^{++} + \text{OH}^- + \text{H}^+ + \text{SO}_4^{--}$
- 5)  $\text{Mg}^{++} + \text{H}_2\text{O} + \text{SO}_4^{--}$

This process is made plausible by the fact that the first  $\text{H}_2\text{O}$  molecule entering between the two bivalent ions is strongly deformed because of electrostatic forces so that the dissociation of the complex is much more probable than that of  $\text{H}_2\text{O}$  in the free medium. The first step (1-2) may occur very quickly but anyway is not acoustically effective since the resulting big univalent ions have only a small hydrate shell and therewith only a small change in volume is caused. The next step (2-3) or perhaps the total step (1-3) is assumed to occur in a time smaller than  $10^{-9}$  s thus causing the increase of  $Q\lambda$  towards high frequencies while step (4) takes about  $10^{-6}$  s and may cause the absorption maximum at 130 kc/s. Steps (3) and (4) both are coupled with a considerable change in volume because of the formation of the big hydrate shells of the bivalent ions and therefore the equilibrium can be influenced by the sound pressure. Due to the anomalous mobility of the  $\text{H}^+$  and  $\text{OH}^-$  ions the last step (5) occurs very quickly and may be left out of consideration in this connection.

With this model, the amount of the absorption depends on the number of undissociated molecules, which is proportional to the concentration in the above mentioned range, i.e. the absorption cross-section must be independent of concentration as is the degree of dissociation. The model



further explains both relaxation processes at a time. The observations made when adding acids or alkali and the behaviour of mixtures can be easily understood if the change in degree of dissociation and activities caused by the admixture is taken into account. Especially the above given empirical mixing rule for mixtures  $\text{MgSO}_4 + \text{NaCl}$  (5, b,  $\gamma$ , iv) can be explained quantitatively by the formation of  $\text{NaSO}_4^-$  ions, the degree of dissociation of which is very low [47].

The model can be applied analogously to all 2-2-valent salts investigated. In the case of the salts of minor valency a similar process may occur, but more probably a dissociation in one step causes the absorption. In this case only conjectures can be made because the maximum of  $Q\lambda$  always is above the frequency range and could not be determined.

#### d) Comparison of the attempted explanations

Both the models of the structural relaxation processes discussed are unsatisfying because of the additional physico-chemical assumptions necessary. With the hydration model most of the results are easy to explain, while difficulties arise in the case of 2-1-valent salts and the behaviour of mixtures. The association model, especially suggested from the measured results with the mixtures, seems somewhat doubtful because of the high degree of association required, which is in contradiction to the usual assumptions in physical chemistry. Together with the thermal relaxation model it is applicable to nearly all measured effects, except the influence of the  $p$ -value on the absorption, and the absorption measured with  $\text{Mg}(\text{OH})_2$ . The chemical relaxation model discussed, which in general leads to similar results to the association model, gives a plausible explanation in this case too, and therefore at the moment seems to be the best model for the origin of the sound absorption in electrolytic solutions.

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